# UNITED STATES DEPARTMENT OF THE INTERIOR GEOLOGICAL SURVEY

# GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS (formerly Geochemical Survey of the Western Coal Regions)

Third Annual Progress Report, July 1976

Ву

U.S. Geological Survey Denver, Colorado

Open-file Report 76-729 1976

This report is preliminary and has not been edited or reviewed for conformity with U.S. Geological Survey standards or nomenclature



# GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS (formerly Geochemical Survey of the Western Coal Regions) July 1976

Third annual progress report describing current work in a broad-scaled reconnaissance geochemical study of landscape materials in the major coal-, uranium-, and oil shale-bearing lands of the western United States.

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The term "statistically significant" appears often in scientific literature--notably and sometimes confusingly in sampling studies that hold implications for public policy. Understanding its narrow meaning, as an element in the interpretation of degrees of scientific proof, is essential to grasping the import of a scientific state-ment bearing on public policy.

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Generally, a sampling result or experimental result is deemed "statistically significant" when the calculated probability of its being solely an artifact of chance is below a specified low value. Many scientists disagree on what that low value should be. Customarily, many regard as "statistically significant" a result for which the probability of occurrence as a consequence of pure chance is less than five percent (the "0.05 probability level"). This concept is intended to reduce the likelihood that a result may be interpreted as attributable to factors under study when it may be, in fact, the happenstance of a random distribution.

(Adapted from the National Academy of Sciences' "News

Report, "Mid-June, 1976, v. XXVI, no. 8, p. 6)

#### WORK TO DATE

This is the third in a series of annual reports describing field studies in environmental geochemistry of the western energy regions. While the original focus of the work was on coal (and our primary interest remains there), the work has been expanded to include studies in the oil shale region of western Colorado, northeastern Utah, and southwestern Wyoming. In the oil shale work, we have established a fruitful working relationship with Ronald W. Klusman and Charles D. Ringrose of the Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado. Further, because the western United States contains economic quantities of uranium as well, we intend to begin assessing the geochemical impact of uranium mining and milling on the trace-element character of the landscape. Field work, underway or completed in all these subject areas, is summarized in figure 1.

Work in the Powder River Basin is nearly complete. Most of the field collections throughout the Northern Great Plains are complete, although much of the laboratory analysis has not yet been received. A few studies have been initiated in the oil shale region and in Wyoming basins other than the Powder River Basin. Field collections adjacent to four coal-fired, electric generating plants are complete although, again, not all of the laboratory results have been received.

Background geochemical studies in rocks, soils, sediments, vegetation, and water constitute the core of our work in the western energy regions. Collectively, they comprise an attempt to define and quantify the regional geochemical background or "baseline" in the area. We have found it useful to define a geochemical baseline in terms of a reasonable range of a chemical property rather than a single value (U.S. Geological Survey, 1974b, p. 6-13; Tidball and Ebens, 1976). In fact, given the geochemical variability inherent in the natural landscape, a variety of summary properties may be of use in measuring or monitoring geochemical change. Some of these are discussed on the inside cover of this report.

Summary data of various kinds occur throughout the body of this report, and collective summaries of probable upper limits of element concentration expected in a variety of landscape materials in the Powder River Basin, the Northern Great Plains, and the Oil Shale Region are given in Appendices I, II, and III. Such limits, although informative of natural geochemical conditions, are of limited use in establishing trace-element hazards. A chemical hazard is a difficult concept to define, but however defined, a fairly extensive survey of the literature in Appendix IV strongly suggests that an element hazard cannot be identified without reference to a specific plant or animal type.

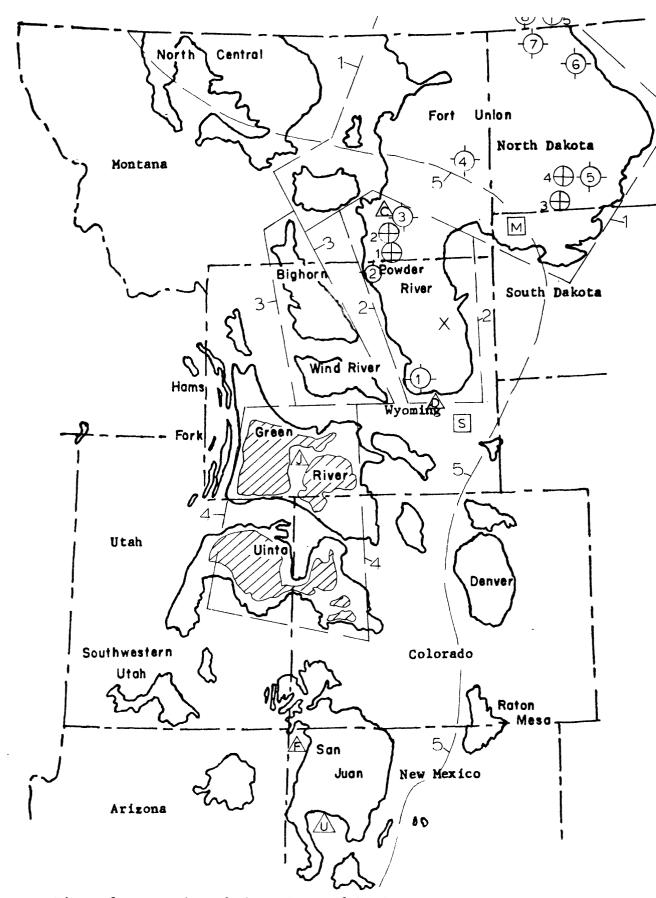


Figure 1. Location of the major coal basins in the western United States (modified from Trumbull, 1960). Approximate distribution of Green River Formation is cross-hatched.

### Figure 1 -- EXPLANATION

Map unit	Material sampled	Reference
1. Northern Great	Sandstone, shale Soil Stream sediments Ground water Wheat	This report, p. 10-13, 94-100 This report, p. 57-81 This report, p. 14-21 This report, p. 86-93 This report, Appendix II.
2. Powder River Basin	Sandstone, shale Soil, soil parent, sagebrush, lichen, grass	This report, p. 10-13, 94-100 (See U.S. Geol. Survey, 1974, 1975; Connor, Keith, and Anderson, 1976; Tidball and Ebens, 1976.)
	Sediments (Powder River)	This report, p. 30-36
3. Bighorn, Wind River Basins	Soil	(No data as yet)
4. Oil Shale Region	Oil shale Soil Stream sediments	This report, p. 48-56 This report, p. 101-111 This report, p. 121-130
5. Western United States	Sagebrush (west of line)	(No data as yet)
	Strip-mine spoils, sweetclover,	This report, p. 4-9, 82-85
<b></b>	wheatgrass Mines: 1. Dave Johnston; 2. Welch; 3. Big Sky: 4. Savage; 5. Beulah; 6. Velva; 7. Kincaid; and 8. Utility.	(See U.S. Geol. Survey, 1975)
$\oplus$	Shale, cored overburden (Cores: 1. Bear Creek; 2. Otter Creek; 3. Dengate; 4. Dunn Center; 5. Estevan.)	This report, p. 10-13
X	Ground water	(See U.S. Geol. Survey, 1974, 1975.)
	Vegetation (S, sagebrush; M, mixed feed grains)	(No data as yet)
$\triangle$	Coal-fired powerplants (C, Colstrip; J, Jim Bridger; D, Dave Johnston; F, Four Corners).	This report, p. 22-29, 37-47, 112-120. (See also U.S. Geol. Survey, 1974, 1975; Connor, Keith, and Anderson, 1976)
$\triangle$	Uranium mill	(No data as yet)

# MOLYBDENUM IN SWEETCLOVER GROWING ON MINE SPOILS by James A. Erdman and Richard J. Ebens

#### Introduction

New environmental regulations governing the strip-mining of coal on federally owned lands in the West contain mining and reclamation performance standards designed to insure that miners leave the land in at least as good condition as they found it (Holden, 1976). The area of the Northern Great Plains within the lignite and subbituminous regions is predominantly rangeland although dryland cropping--principally small grain production--is also an important agricultural activity. Thus, the intent of these reclamation standards is to assure the rehabilitation of surface-mined lands for agricultural production, providing such areas had been rangeland or cropland before mining began.

Most assessments of the possible geochemical alteration of surfacemined lands deal with revegetation problems; that is, attempts to provide plant cover as quickly as possible in order to minimize soil erosion. (See, for example, Sandoval and others, 1973; Berg and Vogel, 1973.) Such problems are of immediate and valid concern, but altered physical properties or changes in trace element concentrations that may prove deleterious or harmful to livestock ranging on the reclaimed lands must also be considered. Because of our experience with adverse effects of a clay-mining operation on cattle in Missouri (Ebens and others, 1973), we set out to examine the element composition of coal-mine spoil materials and sweetclover (Melilotus officinalis (L.) Lam. or M. alba Desr.) from eight selected coal mines in the Northern Great Plains. Some preliminary results of that study are given in U.S. Geological Survey (1975, p. 29-35). Whereas the main purpose of this study was to assess the degree of differences and similarities for a large suite of elements among the eight mines, our intent here is to describe the potential of sweetclover that grows on spoil materials as a causative agent of molybdenosis in certain livestock.

Coal-mine spoils are geochemically anomalous when compared to naturally occurring surficial materials (Sandoval and others, 1973). Despite the increasing practice of top-soiling contoured spoil banks, we find evidence that these anomalies are being reflected in the element composition of vegetation that grows on this modified substrate. This appears to be the case at least for sweetclover, which is a common and often dominant plant over many of the spoil banks in the Northern Great Plains.

Molybdenosis is a copper-deficiency disease that is well-documented in cattle and sheep; in the latter case, it is called swayback disease of lambs (Alloway, 1973). Generally, excessive amounts of molybdenum in the diet result in a decrease in the physiological availability of copper. Characteristic symptoms in cattle are scouring, weight loss, loss of pigmentation, and in some cases, breeding difficulties. Calves are most susceptible, the effects often being irreversible (Barshad, 1948). Horses are reported to be unaffected.

The total molybdenum in soil where cattle have been known to be affected is not high, ranging from 1.5-10 ppm in the study described by Barshad (1948). In alkaline soils, however, a large percentage of this element may be soluble in water. Barshad (1948) stated, "Growing plants, particularly legumes, are able to absorb amounts of molybdenum harmful to cattle from soils that contain as little as 1.5-5.0 ppm total Mo."

The proportion of copper to molybdenum in the forage is considered to be more critical than the total amount of molybdenum in either the soil or plants. Copper-to-molybdenum ratios of about 5:1 or less in winter herbage from the British Isles have caused swayback in lambs and hypocuprosis in cattle (Alloway, 1973). A copper-to-molybdenum ratio of about 7:1 is apparently optimum for cattle, according to the University of Missouri's veterinary toxicologist, A. A. Case (written communication, 1974). Similar ratios were cited by Alloway (1973) for control farms. Clearly, where legumes are a substantial part of the pasturage in molybdic and alkaline soils, certain types of livestock can be severely affected.

Concern over the possible incidence of molybdenum-induced imbalances in animals grazing in regions associated with coal utilization is not new, although more information seems to be available on the effects of fly ash on the content of forage than on the effects of coal-mine spoils (Furr and others, 1975; Gutenmann and others, 1976). The only documented case of molybdenosis in cattle from the western coal regions is the report by Christianson and Jacobson (undated), which describes an area where uraniferous lignite was burned in rotary kilns in order to concentrate the uranium, and the molybdenum in the ash contaminated the surrounding pasturage. The most recent interest in molybdenum-related nutritional problems was expressed by Martens and Beahm (1976) who cautioned, "Molybdenum availability of some fly ashes is sufficiently high that levels in plants grown on fly-ash soil mixtures can be hazardous to grazing animals."

There are reasons for our interest in sweetclover and its molybdenum-accumulating potential other than its abundance and widespread occurrence on the coal-mine spoils that we studied. Legumes are recommended in seed mixes for reclamation because of their nitrogen-fixing capabilities, and sweetclover, in particular, is considered one of the more suitable plant species for spoil bank stabilization. Finally, the forage value of sweet-clover rates very high. According to A. A. Case (written communication, 1975), "Sweetclover is a wholesome and very nutritious legume, ranking along with other clovers in its nutritional value, perhaps just less than alfalfa, which is considered the 'queen' of legumes for forages and hay purposes." Although under most circumstances, sweetclover is not considered a toxic plant, Case does warn of changes that can occur where it grows in altered environments.

#### Methods

Sampling design .-- Field work was undertaken during late summer of 1974 with sampling conducted according to a two-level analysis of variance Samples of sweetclover and associated soil and/or spoil material were collected from 10 randomly selected sites (in which sweetclover could be found) at each of eight surface mines scattered throughout the Northern Great Plains. Mine locations are shown on figure 1 and minespoil descriptions are given in our initial report (U.S. Geological Survey, 1975, p. 33-34). A channel sample of spoil material or a spoilsoil mixture (where topsoiling had been attempted) was collected to a depth of about 20 cm. The sweetclover sample consisted of the aboveground portion of a plant growing within 1 m of the soil sample. sufficient amount of plant material was unavailable from a single plant, more was composited from an area of as much as 10 m<sup>2</sup>. We tried to sample only yellow sweetclover (M. officinalis) in its flowering and early fruiting stage with abundant leaf tissue, but some samples were further developed and had a greater proportion of stem tissue. At the Big Sky Mine and the Utility Mine, plants of yellow sweetclover had matured to the point where mostly only stems remained; therefore, the later-maturing white sweetclover ( $\underline{M}$ .  $\underline{alba}$ ) was substituted. Both species occurred at most mines, although yellow sweetclover appeared to be more abundant. A small suite of yellow sweetclover samples taken from presumably unmineralized sites located across the conterminous United States was submitted for analysis to serve as a control or baseline data set.

Analytical methods.--Sweetclover samples were first dry ashed at 450°C for 24 hours. Copper analyses were performed by T. F. Harms using atomic absorption spectrophotometry (Nakagawa, 1975).

C. S. E. Papp conducted the molybdenum determinations using the thiocyanate method of Reichen and Ward (1951). Because many reports on element concentrations in sweetclover are given on a dry-weight or moisture-free basis (for example, Furr and others, 1975), we have converted the element concentrations that are reported on an ash basis by the analysts to a dry-weight basis, using the following formula:

$$X_d = X_a \cdot X_p/100$$
 ,

where  $\mathbf{X}_d$  is the concentration in the dry material of the sample,  $\mathbf{X}_d$  is the concentration in the ash, and  $\mathbf{X}_d$  is the percent ash in the dry material.

Samples of spoil materials were ground to pass through an 80-mesh sieve. Because of the relatively high content of organic carbon in some samples, all samples were asked prior to analysis of all but the volatile elements. Soil pH was measured by a hydrogen ion-specific glass electrode in a water-saturated paste.

#### Results and discussion

Concentrations of copper and molybdenum were transformed to a logarithmic scale prior to evaluation because their frequency distributions were more nearly symmetrical on a logarithmic scale than on an arithmetic scale. Under these circumstances, the geometric mean (GM) is the best estimate of the most probable metal concentration. The geometric deviation (GD) is a factor expressing the degree of total variability measured. The expected 95-percent range given for the baseline data estimates the range that 95 percent of a suite of randomly collected samples from normal environments should exhibit. Anomalous concentrations are those that lie outside this range. The estimated range of the central 95 percent of the observed distribution has a lower limit equal to  $\underline{\rm GM}/(\underline{\rm GD})^2$  and an upper limit equal to  $\underline{\rm GM}/(\underline{\rm GD})^2$ .

Table 1 lists the summary statistics for copper and molybdenum in sweetclover, and the pH of the spoil material. Because of the importance of the Cu:Mo ratio, we have ranked the mines in increasing value of the ratio. Analysis of variance tests demonstrate significant differences (p<0.05) among the mines for all four variables; but a multiple range test (Duncan, 1955) failed to group the means further, with the exception of molybdenum in sweetclover. Results of the test revealed two distinct groups of sweetclover with respect to its molybdenum content. The Beulah, Dave Johnston, and Welch mines comprised one group with means ranging from 2.6-3.4 ppm Mo in dry material, and the other five mines comprised the other group with means ranging from 6.4-13 ppm.

In comparing the statistics between the mines and the baseline data, it is apparent that the concentrations of copper in sweetclover and the levels of pH in the mine samples and baseline samples are not notably different. However, certain sweetclover samples from several mines show unusually high molybdenum contents and unusually low Cu:Mo ratios. Half of the samples from both the Big Sky and Utility mines had ratios below baseline (the expected 95-percent range). Many spoil samples from all mines are either anomalously high or low in pH.

Even more important, mines having the lowest molybdenum averages in sweetclover are the same mines with decidedly lower pH in the spoil materials. Inasmuch as molybdenum is often much more available to legumes where soils are alkaline (Case, 1974), we computed the correlation between the concentration of molybdenum in sweetclover and the pH levels in the associated spoil materials. The resulting correlation coefficient--0.46--is significant at the 0.01 probability level, although it does not indicate a particularly strong relationship.

Finally, a test was made of differences in copper and molybdenum concentrations between yellow and white sweetclover based on paired samples collected at each of 12 sites (cf. U.S. Geol. Survey, 1975, p. 31). The two species varied significantly in their molybdenum content at the 0.05 probability level but not in their copper content. White

Table 1 .-- Copper and molybdenum in sweetclover (Melilotus spp.), and pH in spoil materials from eight coal mines in the Northern Great Plains

million in dry material; arithmetic mean (AM) of pH expressed in standard units; GD, geometric deviation; SD, standard deviation; mines listed in order of increasing Cu:mo ratios] [Geometric mean (GM) concentrations and observed ranges expressed as parts per

			Swee	tclover	, abov	Sweetclover, above ground parts	rts				Mine spoils	poils
		Copper			Molybdenum	enum		Cu:Mo ratio	ratio		Hd	
Mines, or baseline data	GM	<u>GD</u>	Observed range	MS	<u>ap</u>	Observed range	NS I	<del>as</del>	Observed range	AM	<u>SD</u>	Observed range
Big Sky	8.2	1.16	6.5-9.8	13.0	1.23	10-20	19.0	1.21	٥٠٠٤ - 0.75	9.7	0.53	6.5-8.5
Utility	6.9	1.14	5.3-9.0	7	1.33	6.4-18	.62	1.29	.43-1.0	7.8	1.30	4.4-9.0
Velva	7.2	1.18	5.9-9.5	4.9	1.25	5.3-12	.92	1.27	4.1-69.	7.8	04.	7.0-8.5
Ѕвувде	5.9	1.27	4.1-9.3	4.9	1.30	4.8-10	8.	1.47	.50-1.9	8.2	64.	7.0-8.5
Kincaid	0.6	1.20	6.7-13	6.5	ਲੈ.ਜ	2.8-18	1.1	1.70	.65-2.8	7.8	.71	7.1-9.4
Beulah	5.5	1.14	2.9-4.4	5.6	1.60	1.2-8.3	2.1	1.60	.63-3.8	7.0	69.	6.2-8.7
Dave Johnston -	7.0	1.19	5.2-9.5	3.1	2.18	1.5-14	2.3	2.34	47-6.5	6.2	1.59	4.0-8.5
Welch	8.1	1.27	5.6-11	3.4	1.68	1.9-9.5	7.2	1.77	1.2-5.0	9.9	%	5.4-7.8
Baseline data2/	9.7	1.66	2.8-21]	2.1	2.57	,32-14 <sup>1</sup> √	3.6	2.35	.65-201/	7.2	94.	$6.3-8.1^{1/3}$

<sup>1/</sup>Ranges given for baseline data are not the "observed" ranges, but the expected central 95-percent ranges as described in the text.

<sup>2/</sup> Sweetclover baseline based on eight samples collected throughout the United States; pH baseline based on 64 A-horizon soil samples collected across the Powder River Basin (Tidball and Ebens, 1976).

sweetclover contains almost twice as much molybdenum as does yellow sweetclover; their copper contents, on the other hand, are about the same. Similar comparisons by Barshad (1948)--although not based on paired observations--also indicated that white sweetclover accumulates more molybdenum than does yellow sweetclover. Despite the significant differences between sweetclover species, the multiple group test (Duncan, 1955) did not separate the Big Sky and Utility mines where we collected white sweetclover from those where we collected yellow sweetclover. Moreover, spoil at most mines that we sampled supported both species.

### Conclusions

Molybdenum concentrations in sweetclover growing on coal-mine spoil banks in the Northern Great Plains are probably sufficiently high to induce metabolic imbalances in cattle and possibly sheep in subclinical, if not acute, levels, assuming the animals were to feed predominantly on this legume. Alloway (1973) considered that a copper to molybdenum ratio less than five may induce swayback in sheep and hypocuprosis in cattle; the ratios of these elements in sweetclover from the mines in this study are considerably below this threshold. A tolerance level for cattle of five ppm molybdenum in dry forage (Webb and Atkinson, 1965) is exceeded by sweetclover at all but the Beulah, Dave Johnston, and Welch In mine areas where molybdenosis may be a potential problem, wholesome pasturage can be established by avoiding molybdenum-accumulating plant species, or by minimizing access to the fresh forage which can cause greater injury than properly cured material (Barshad, 1948). Molybdenum-induced copper imbalances in the diet may also be prevented by treating the affected livestock with either copper sulfate or copper glycinate.

It may be difficult, if not impossible, to prevent potentially hazardous geochemical environments in some surface-mining operations. But with the proper management of reclaimed areas, mining need not be precluded.

# MINERALOGY OF FINE-GRAINED ROCKS IN THE FORT UNION FORMATION by Todd K. Hinkley and Richard J. Ebens

The rearrangement of rock strata during mining and reclamation commonly exposes originally buried strata to weathering processes which may accelerate chemical release. Shale or mudstone is the most abundant rock type in coal overburden in the Northern Great Plains Coal Province and is most likely to appear as a major constituent of a reclaimed landscape. A knowledge of the mineralogical variability of this rock type may lead to a better understanding of the environmental needs for handling such strata during, or following, strip mining.

The most prominent aspect of mineral variability in these rocks is, of course, reflected as vertical changes among the strata comprising the overburden at any given location. A second and perhaps equally important aspect is the change from place to place over the province of some average mineral property of the overburden column. This second aspect is largely obscured by the magnitude of the first. Nevertheless, the distinctive chemical differences that have been noted in sweetclover substrate among eight strip mines (U.S. Geological Survey, 1975, p. 29-35) suggest that such overburden may vary in its mineralogy in a geographic as well as a stratigraphic sense.

The present report describes an attempt to quantify the magnitude of this geographic variation in these rocks. A suite of fine-grained samples was taken from cores drilled through the overburden sections of strippable coal deposits in rocks of the Fort Union Formation or equivalents. These samples have been used to estimate the mineralogical variation of the fine-grained rocks over two geographic and one stratigraphic scales: 1) distances greater than 5 km, 2) distances from 0-5 km, and 3) distances across the rock column of less than 100 m (stratigraphic variation).

### Sample sites and sampling design

Samples were taken from each of five widely separated sites (>50 km), two in southeastern Montana, two in southwestern North Dakota, and one in southeastern Saskatchewan (fig. 1). At each site, four rock samples were taken from each of two drill holes which were separated by 1-5 km. The samples taken from each core were stratigraphically separated by 0-100 m and consisted of 30 cm of a homogeneous stratum of shale or mudstone. Only three samples were collected from each of the two drill holes at Estevan, Saskatchewan, because of the paucity of fine-grained horizons in these cores. In all, 38 samples were collected. Twelve samples were split and submitted in duplicate to test analytical reliability as distinct from geographical variability, bringing the number of actual analyses to 50.

Cores from three of the five sites (Bear Creek and Otter Creek, Montana, and Dunn Center, North Dakota) were obtained through the

Energy Minerals Rehabilitation Inventory and Analysis (EMRIA) program of the U.S. Bureau of Land Management, which program is intended to gather a variety of environmental information at potential coal-mining sites. Cores from Dengate, North Dakota were obtained from C. S. V. Barclay of the Conservation Division, U.S. Geological Survey. Cores from Estevan, Saskatchewan were obtained from the Industrial Minerals Division, Department of Mineral Resources, Saskatchewan.

### Analytical methods

Samples were semi-quantitatively analyzed for mineral composition by an X-ray diffraction method similar to that described by Schultz (1964). The rocks were crushed in a jaw crusher and then ground in a vertical Braun pulverizer with ceramic plates set to pass 80 mesh. These were further ground in an agate mortar for three minutes. Final sample preparation and diffractograms were done by D. Gautier, using a slit width continuously variable with  $2\theta$ . The mineral concentrations are summarized in table 2.

### Scales of variation

Regional variation. -- Three of the mineral constituents (quartz, kaolinite, chlorite) exhibit significant variation at the highest geographic, or regional, level, indicating the existence of truly regional and possibly mappable mineralogical and chemical trends in the Northern Great Plains. These regional differences may be due to broadscale differences in the environments of deposition, broad-scale hydrologic regimes, or even secular or fossilized weathering effects. In addition, plagioclase, dolomite, and calcite, vary significantly at the regional level when the top level variance is compared with two or more of the lower levels combined (pooled variance). From the small amounts of chemical data available to date in this study, it is clear from a basic comparison of mean abundance values by region that the values for plagioclase (and one of its chemical constituents, Na20) are highest at the same two sites, Dengate, South Dakota and Estevan, Saskatchewan. Similarly, dolomite and MgO are highest at the same site, Otter Creek, Montana.

Local variation.--Essentially no mineralogical variation exists between the paired holes (1-5 km separation) within the individual sites. This indicates that the mineralogy (and presumably chemistry, also) is consistent in overburden over areas approximately the size of a strip mine in this part of the western coal regions. If the geochemical properties at this scale are as uniform as the mineralogical, then chemical characterization of such rocks over areas a few kilometers across becomes a relatively easy matter. For example, detailed analysis in only two or three scattered cores should suffice, and large (and expensive) drilling programs may be mostly wasted effort. Variation among samples taken across the strata (within the cored sections) is large compared to the other components of variation as is expected in layered rocks.

Table 2 .-- Statistical summary of the mineral composition of fine-grained rocks cored

[\*, indicates significance of the variance component at the 0.05 probability level; p, indicates significance of a pooled variance] from the Ft. Union Formation, Northern Great Plains Coal Province

			Components as percent of total variance	as percel	nt	, , , , , , , , , , , , , , , , , , ,	Summary statistics	tistics	
Mineral constituent	Total log <sub>10</sub> variance	Among	Between	Among samples	Between analytical duplicates	Geometric mean (percent)	Geometric deviation	Minimum	Maximum
Quartz	0.0254	34.9*,p	0*0	59.2	5.9	25.7	1.44	14.0	0.64
Plagioclase	6680°	28p	0.0	57.1*	14.9	3,51	1.99	#	10
K-feldspar	.0767	<b>8.</b> 4	0.0	15.4	7.67	1,65	1.89	< .25	9
Total clay	.0225	16.2	0.0	75.8*	<b>∞</b>	47.2	1,41	12	80
Kaolinite	1.181	584,p	0.0	41.9*	.1	5.20	12.2	< .25	80
Chlorite	.492	56.9%,p	0.0	45.7	7.	18.5	5.03	< .25	65
Dolomite	.552	21.5p	0.0	55.9*	22.6	1.56	5.54	< .25	33
Calcite	.356	14.7p	0.0	41.8	43.6	.73	3.95	< .25	10
Siderite	.335	7.9	0.0	65.1*	27	99*	3.79	< .25	20
Mixed carbonate ,195	ite .195	0.0	<b>6.</b> 4	93.6*	0.0	.31	2.77	<ul><li>25</li></ul>	22
					The state of the s				

Analytical variation. -- For several of the minerals determined, major variation occurs at the fourth or analytical level. This represents a lack of consistency between analytical duplicates and is due in part to proximity of key mineral peaks on the diffractograms. In general, for the rocks of this study, the minerals which are present in the lowest concentrations (K-feldspar, carbonates) are the ones most affected by analytical variation. They are the most sensitive to chart-reading errors, which yield mineral abundance errors of high fractional magnitude, whereas those present in highest concentrations (clays, quartz) are the least affected.

### Mineralogy of the rocks

Quartz, the two carbonate minerals calcite and dolomite, and the two clay minerals kaolinite and chlorite, all vary regionally, and the abundances for each mineral between the high and low sites may be compared. Judging by the geometric means at individual sites, quartz is at a maximum at Otter Creek, Montana (geometric mean of 31.6%) and a minimum at Dengate, North Dakota (19.1%). Calcite and dolomite have their highest geometric means at Otter Creek, Montana (values of 1.76% and 6.04%, respectively) and lowest geometric means at Dear Creek. Montana (0.35% and 0.39%). Total clay does not vary regionally, but its two main constituents in the mineral scheme of this study, kaolinite and chlorite, show regional variation. The site highest in chlorite, Estevan, Saskatchewan (geometric mean of 52.3%), is also the one lowest in kaolinite (0.96%). Bear Creek, Montana is both lowest in chlorite (GM of 1.8%) and highest in kaolinite (39.6%). In the absence of evidence for different authigenic processes in the various sites, this observation of an inverse abundance pattern for the two clays in these fine-grained rocks indicates different provenances for the different sites. A regional variation in a clay ratio of this sort may well result in a distinctive distribution of elements held in those clays.

The distribution patterns for siderite and "mixed carbonate" (probably ankerite), the two minor carbonates of the mineral scheme, are too irregular to be considered in the same manner as the other minerals. Both are totally absent from most samples, and "mixed carbonate" is present only at Dengate, North Dakota and Estevan, Saskatchewan.

# STREAM SEDIMENT CHEMISTRY IN THE NORTHERN GREAT PLAINS by James M. McNeal

One expected geochemical impact of large-scale, coal-based, energy development in the western United States is a change in the mineral and chemical character of the sediment in streams draining strip-mined areas. As with other components of the geochemical landscape, if such expected changes are to be monitored, a regional background or baseline must first be established. A necessary prerequisite to establishing such a baseline in an efficient manner, however, is concrete knowledge of the geographic scale of variation in those sediments. This study was undertaken to provide such information using a specific size fraction of stream sediments from the Northern Great Plains. Preliminary results for eight chemical properties are presented here.

There are two objectives of this study. The first was to determine whether or not stream order and size of drainage basin are important parameters in defining different populations of sediments, and the second was to determine the magnitude of the regional geochemical variability of the sediments. To this end, data collected to date were analyzed in two analysis of variance designs.

Three target populations were defined: sediments in first, second, and third order streams, as shown on 1/1,000,000 scale topographic maps. A first order stream is an upstream, unbranched stream segment; a second order stream extends downstream from the junction of two first order streams; a third order stream extends downstream from the junction of two second order streams (Strahler, 1969). Streams larger than third order were not studied because they were too few in number. In addition to stream order, the size of the drainage basin above each sample location was measured in order to investigate its relationship to the element content of the sediment. Ten randomly selected 50 km<sup>2</sup> areas were chosen from a total of 15 in the Northern Great Plains which contained at least two streams of each of the three stream orders of interest. The sample locations and areas are shown in figure 2. Two streams of each of three orders were then randomly selected. Further, one stream of each order was randomly selected and a second sample taken approximately 100 m upstream from the first. In order to reduce the sampling error, all samples were composited from 5-9 grab samples, depending on the size of the stream. All localities were sampled as near to the junction of the target stream and a stream of the next highest order as possible, while at the same time, remaining above the region of influence of the larger stream during flood conditions. In all, 90 stream sediment samples were collected (10 areas, 3 stream orders per area, and 3 samples per order); 20 of these were selected randomly and split into two parts to provide an estimate of analytical error. The resulting 110 samples were placed in a random order, sieved to less than 100 mesh, and submitted for analysis.

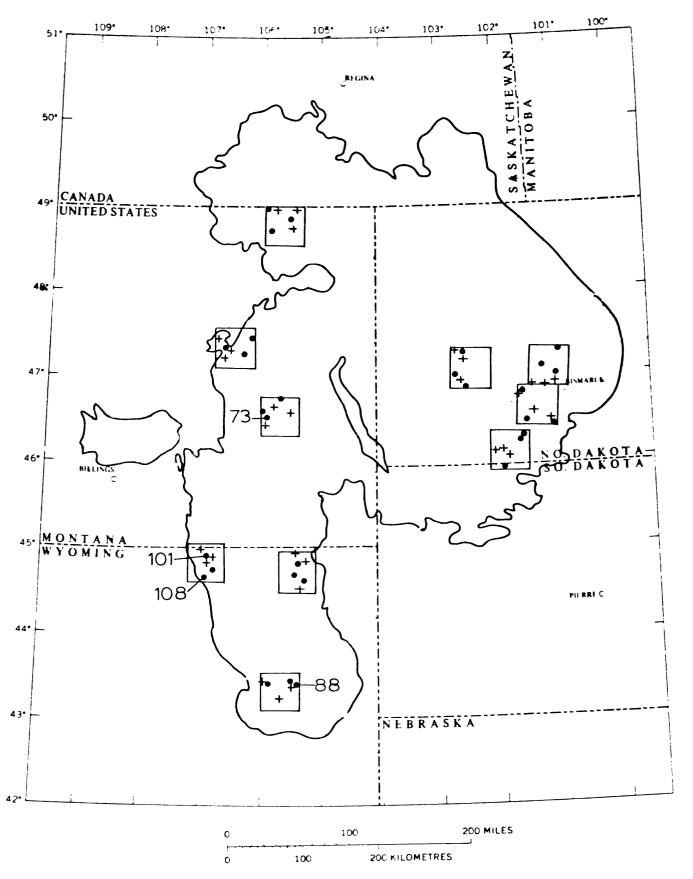


Figure 2.--Stream sediment sampling localities (dots and pluses) in selected areas of the Northern Great Plains. Solid dots indicate samples used in chemical extraction studies. Numbered samples are referred to in the text.

### Sample Collection and Preparation

All samples were collected by hand or with a "fox-hole shovel" from wet or "active" portions of the streams (some localities on the smaller streams were dry), being careful to exclude any material that was in contact with the shovel. Approximately 1 to 3 kg of material was collected per sample, depending on the proportion of fines available. All samples were placed in cloth bags and, if the cloth bag was oozing water, into polyethelene bags. Sediments in cloth bags were allowed to air-dry. Water was poured from the polyethelene bags as it accumulated. When no further water accumulated, the cloth bag was removed and allowed to dry, as above.

After drying in an oven at approximately  $40\,^{\circ}\text{C}$ , the material was removed from the bag and disaggregated in a ceramic mortar with a pestle on a drill press. Care was taken to insure that the particle size was not reduced. The material was sieved in a stainless steel sieve and a sieve shaker. The greater than 100 mesh (greater than 150 micron) size fraction was discarded.

The procedures by which the samples were analyzed are given in U.S. Geological Survey (1975), but only results for C-total, Li,  $Na_2O$ , MgO, Rb, Th, U, and Zn are reported here. The analyses were performed by J. Crock, Lorraine Lee, Hugh Millard, W. Mountjoy and V. E. Shaw. The drainage area of each sample location was determined by using a polar planimeter.

### Results and Discussion

The data from each stream order were analyzed by a nested one-way analysis of variance design in which: (1) differences among the 10 areas (shown in figure 2) constituted the regional effect, (2) differences between the two streams (of each order) within the areas constituted the effects at intermediate geographic scales, (3) differences between samples within each locality constituted the sampling error, and (4) differences between splits constituted the analytical error.

The results in table 3 show that much of the geochemical variance is associated with the between-streams level (within-area level) for each of the eight constituents. Particularly large amounts of the variance of Log MgO, Log Na<sub>2</sub>O and Log U occur at the between-area level, and except for Log C and Log U, little variation was found at the sampling level. Thus, compositing of samples at a site within a locality substantially reduced the variance effects expected at this level.

Table 3.--Geochemical variation in stream sediments of the northern Great Plains.

[An asterisk (\*) indicates that the variance component is significantly different from zero at the 0.05 probability level. Data in parts per million, except where given as percent]

			Variance			ent of total		Summary sta	
Constituent	Stream order	Total Log variance	Petween areas	Between streams	Sampling error	Analytical error	Geometric mean	Geometric deviation	Expected 95% range (baseline)
C(total), %	1	0.0738	26	584	16*	<1	2.2	1.87	0.64-7.9
	2	.0277	<1	51	49*	<1	2.6	1.47	1.3-5.2
	3	.0203	11	60 <sup>)</sup>	29*	<1	1.7	1.39	.88-3.3
Li	1	.0095	<1	92*	5	3	]		
	2	.0055	<1	91*	7*	2	19	1.21	13-27
	3	.0042	7	85*	2	6	J		
Na <sub>2</sub> O, %	1	.0706	66*	22*	<1	12	]		
	2	.0979	93*	7*	<1	<1	.96	1.93	
	3	.0770	76*	24*	<1	<1	]		
Mg0, %	1	.0132	15*	21	<1	64	1.59	1.30	
	2	.0251	55*	42*	4*	<1	1.84	1.44	
	3	.0263	87*	13*	<1	<1	1.64	1.45	
Rb	1	.0070	33	50*	2	15	1		
	2	.0064	20	64*	3	13	70	1.19	49-99
	3	.0031	20	72*	<1	8	]		
Th	1	.0405	23	<1	63*	14	]		
	2	.0305	3	<1	<1	97	8.8	1.51	5.2-15
	3	.0249	<1	9	<1	91	]		
U	1	.0734	58*	<1	38*	4	]		
	2	.0292	69*	14	12*	5	3.4	1.40	<b></b>
	3	.0112	15	11	<1	74	]		
Zn	1	.0075	12	51*	16	22	1		
	2	.0084	<1	28	<1	72	71	1.24	50-100
	3	.0099	19	67*	8	6	}		

A second test consisted of a two-way analysis of variance based on the three stream orders by the ten areas. Two samples were selected in each of the 30 (10 areas by 3 orders) cells in the design. The results are summarized by F-ratios as follows:

				Consti	tuent			
Way	Log C	Log Li	Log MgO	Log Na <sub>2</sub> O	Log Rb	Log Th	Log U	Log Zn
Order (3) Area (10)		1.33 1.04	3.74* 8.61*	0.70 21.6*	0.41 2.84*		1.21 10.76*	1.40 1.74

F-ratios flagged with one asterisk were significantly different from zero at the 0.05 probability level. The results indicate that logarithmic variation for C and MgO is controlled in part by stream order, and they confirm the importance of the broad-scale geographic variation in MgO and Na<sub>2</sub>O and U noted in table 3. Interaction in all constituents was found to be nonsignificant at the 0.05 probability level except for Log U (F = 3.12).

Drainage area seems to have little important relation to logarithmic concentration of any of the constituents studied. Only Li, Rb and Zn exhibit statistically significant covariation with size of drainage area (at the 0.05 probability level) and each is negatively correlated ( $r_{\approx}$ -0.45) with only second order drainages. Provisional baselines for those constituents with nonsignificant regional variance components are presented in table 3. Baseline as used here is defined by Tidball and Ebens (1976) and is computed as outlined on the inside cover of this report.

### Mode of element occurrence

In addition to determining baselines, it is useful to determine the mode of elemental occurrence in the sediments. Such information may be important in assessing the availability of elements to flowing water or to plants. Forty of the 110 samples of  $<150_{11}$ m sediment were chemically leached and each leachate analyzed for Cr, Mn, Ni, Cu, and Zn.

As before, a nested analysis of variance design was used to examine variation at three levels. The three levels are: 1) between 50 km² areas, 2) within areas, and 3) analytical error. Thirty samples were chosen randomly from the ten areas, three per area. Six samples of these 30 were randomly selected to be analyzed in duplicate to provide an estimate of analytical error. Four additional samples were also examined as they were unusual in one or more aspects of their chemistry, but were not included in the analysis of variance design. All 40 samples were analyzed in a randomized sequence.

The following is a list of the chemical extractions in the order performed and the type of sediment material that is expected to be affected. Only the results of the first extraction are complete for the five elements.

- 1. IM sodium acetate, pH 5; extracts easily dissolved minerals and readily exchangeable cations from clays, organic materials, and oxide coatings. The procedure consisted of two treatments each of 24 hour duration with a solution to sediment ratio of 3:1.
- 2. IM hydroxylamine-hydrochloride, pH 2; extracts poorly crystalline or amorphous Mn oxides. This treatment consisted of two successive aliquots of 20 ml of the solution reacting with the sediment from step 1 for 30 minutes.
- 3. 30% hydrogen peroxide; extracts most organic materials and sulfide minerals. To the residue of step 2, 5 ml of 30%  $\rm H_2O_2$  was added. After the reaction ceased the test tubes were placed in a water bath at 65° to 75°C with an additional 5 ml aliquot of  $\rm H_2O_2$  until all reaction ceased. Samples remained overnight in the water bath at about 40°C. The next morning 10 ml of 1M NaOAc, pH 5, was added and the solution was mixed and separated by decanting after centrifuging.
- 4. 0.2M ammonium oxalate, pH 3; extracts poorly crystalline or amorphous Fe oxides. To the residues of step 3, 15 ml of the ammonium oxalate solution was added with mixing. The solutions were stored in the dark for  $2\frac{1}{2}$  to 3 hours. After centrifuging and decanting the solution, an additional 10 ml of reagent was added with mixing. After  $1\frac{1}{2}$  hours in darkness the sample was centrifuged and the two solutions combined.
- 5. 50% nitric acid; dissolves remaining well-crystallized Mn and Fe oxides, also minor attack on clays and other minerals. To the residue of step 4, 20 ml of 50%  $\rm HNO_3$  was added with mixing. The mixture was allowed to sit for 4 hours at room temperature with occasional stirring. Solution was removed after centrifuging the mixture.
- 6. Hydrofluoric, perchloric, and nitric acids; results in total extraction. A .50 gm aliquot of untreated sample is placed in a teflon beaker with concentrated HF and 40% HClO<sub>4</sub>. After heating on a hot plate overnight the solution is evaporated to near dryness and the residue dissolved in a diluted solution of HNO<sub>3</sub>.

Analysis of variance results are shown here for the chemistry of the 1M sodium acetate leachate along with the summary statistics. All data were logarithmically transformed before statistical analysis:

Extracted	Total Log	Variance component (%)			
element	variance	Between areas	Within areas	Analytical variance	
Cr	0.0418	24.2	0	75.8	
Mn	.0447	9.2	88.2*	2.7	
Ni	.0219	0	71.0	29.0	
Cu	.1220	0	66.4	33.6	
Zn	.1700	44.9*	53.9*	1.2	

	Summary statistics					
Extracted element	Geometric mean	Geometric deviation	Geometric error	Expected 95% range (baseline)		
_	0.10	1 (0	1 -1	0.11.00		
Cr, ppm	0.18	1.60	1.51	0.1129		
Mn, ppm	1.70	1.63	1.08	65 <b>-</b> 450		
Ni, ppm	2.8	1.4 <b>1</b>	1.20	1.6-5.0		
Cu, ppm	.32	2.24	1.59	.086-5.0		
Zn, ppm	2.6	2.58	1.11			

Components with an asterisk are significantly different from zero (at the 0.05 probability level). Because Zn exhibits a statistically significant difference between areas, the baseline is expected to vary from place to place within the Northern Great Plains. Except for Cr, all elements exhibit a high (>50%) proportion of the variance at the within-areas level. The high analytical error in Cr, Cu and Ni is probably due, in part, to the fact that the concentrations are very near the detection limit.

Correlation coefficients were computed between the five extracted constituents and the eight bulk constituents discussed previously. Interestingly, no significant ( $_Q$ =.05) correlations were found between any extractable constituent and any total constituent, including extractable Zn vs. total Zn.

In addition to the 36 samples used in the analysis of variance design, four samples of unusual nature were also examined, both by total and extractable analyses:

		Sample number (see fig. 2)				
Extraction	Constituent	73	88	101	108	
Co1d	Cr, ppm	0.2	0.1	0.1	0.2	
Extractable	Mn, ppm	130	30	190	140	
	Ni, ppm	2.8	.8	1.4	1.1	
	Cu, ppm	<b>.</b> 5	.1	.2	.2	
	Zn, ppm	1.4	.7	1.4	9.8	
Total	C-tota1 %	1.63	.69	1.13	2.06	
	Li, ppm	15	2 <b>2</b>	13	10	
	$Na_2O\%$	1.08	.32	.73	1.09	
	MgO %	1.66	1.01	1.32	1.94	
	Rb, ppm	75	95	55	50	
	Zn, ppm	61	86	42	48	

Note that the sample (88) with the highest total Zn (86 ppm) contains the lowest amount of sodium acetate-extractable Zn (0.7 ppm), while the sample (108) with nearly the lowest total Zn (48 ppm) has the greatest amount of extractable Zn (9.8 ppm). The ratio of extractable Zn to total Zn is .20 for sample 108 and .008 for sample 88. The explanation for this major difference may be that the two samples contain greatly differing amounts of MgO and C. MgO is an estimator of clay content and C is probably a fairly good estimator of organic carbon. Both the clays and organic C would serve as hosts for exchangeable Zn. Sample 108 would then have a greater amount of exchangeable sites than would sample 88.

## ELEMENTS IN LICHEN NEAR THE DAVE JOHNSTON POWERPLANT by Larry P. Gough and James A. Erdman

### Introduction

Pacific Power and Light Company's Dave Johnston coal-fired, electric-generating plant is located 8 km east of Glenrock, Wyoming in Converse County near the southern boundary of the Powder River Basin (fig. 3). According to a company brochure, the plant has been in operation since 1958 and burns subbituminous coal in 4 units with a peak capacity of 750,000 KW(e). The mine is located about 15 km northwest of the plant.

Recent studies (Davidson, Natusch, and Wallace, 1974; Lee and others, 1972; Linton and others, 1976) have shown that many potentially toxic trace elements (such as As, Cd, Cr, Ni, Pb, Sb, Se, and Zn) increase in concentration with decreasing particle size of airborne fly ash. These elements associated with the submicrometer fly-ash fraction, as well as Hg, some Se, Cl, and Br, which are discharged as gases (Klein and others, 1975), pass through conventional particulate control devices and are emitted to the atmosphere. Additional evidence that Hg and Se are emitted as vapors or very fine particles, or both, in the flue gas, is provided by the mass-balance studies of Kaakinen and others (1975). They speculate that most of the transition elements analyzed form oxides which volatilize at temperatures below 1,500°C (the near-maximum furnace temperature) and therefore escape through the stacks.

Due to the demand for coal-derived energy, operations similar to the mine-mouth facilities at the Dave Johnston Powerplant have been or are being constructed in the Northern Great Plains. This study reports on the usefulness of the foliose soil lichen Parmelia chlorochroa Tuck. as a natural monitor of powerplant element emissions or related contamination. Results from using big sagebrush (Artemisia tridentata Nutt.) as a monitor, also at the Dave Johnston plant, were given by Connor, Keith, and Anderson (1976).

### Experimental design and data handling methods

Composited samples of <u>P. chlorochroa</u> were collected at approximate logarithmic intervals along east and west transects from the powerplant (fig. 3). Along the east transect six sites were sampled beginning at 2 km and extending to 64 km. Due to the scarcity of the lichen along the west transect, only three sites were sampled—at 2, 4, and 33 km distances. Duplicate samples, taken about 100 m apart and consisting of a composite of many thalli, were collected at each site. Sampling was conducted in September of 1974; however due to the storage of some wet samples, eight were discarded because of decay, and new samples were collected in November, 1974.

All samples were cleaned, dried, and submitted for chemical analyses according to the methods described in U.S. Geological Survey (1975, p. 10-19). The analyses were performed on either the ashed material by emission spectrography and atomic absorption spectroscopy or on the dried material by techniques described in U.S. Geological Survey (1975, p. 74-78).

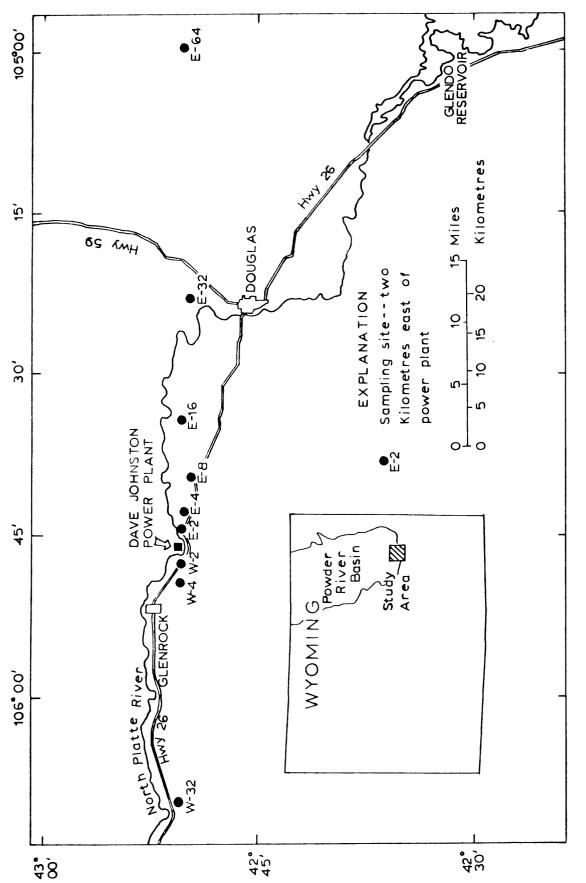


Figure 3.--Map of the study area showing lichen sampling localities east and west of the Dave Johnston Powerplant, Wyoming.

Strong evidence exists that a particular element in plant material may be associated with element emissions when that element decreases in its concentration with increasing distance from an emission source (Connor, Keith, and Anderson, 1976). Linear regression analysis was performed to evaluate this relation in lichen. The regressions were based on a least-squares criterion and prediction equations were calculated using the form:

$$\log_{10} \underline{X} = \underline{b}_0 + \underline{b}_1 \log_{10} \underline{D}$$

where  $\underline{X}$  estimates the concentration of the element,  $\underline{b}_{\underline{0}}$  and  $\underline{b}_{\underline{1}}$  are, respectively, the intercept and slope of the trend  $\lim_{\underline{b}_{\underline{0}}}$ , and  $\underline{b}_{\underline{1}}$  is the distance from the powerplant.

Where  $\underline{b}_1$  was negative (indicating a trend line sloping away from the powerplant) the significance of that slope's deviation from zero (p < 0.05) was estimated using analysis of variance (see, for example, Davis, 1973, p. 192-204). A detailed explanation of this technique when used in point source emission studies is given in Severson and Gough (1976).

### Results

Of 71 elements looked for in samples of <u>P. chlorochroa</u>, 35 were detected in at least some of the samples (Appendix V, table 2). Data for 29 of these elements were adequate for the requirements of regression analysis. Data for the other six elements—Ag, Cd, Co, S, Sb, and Si—were either incomplete or had an unacceptable degree of censoring.

The concentrations of Ca, F, Se, and Sr and ash yield in P. chlorochroa decrease with increasing distance from the Dave Johnston Powerplant and regression statistics for these elements are presented in table 4. The table shows that the slope of the regression lines for F, Se, and Sr was significantly different from zero (p < 0.01). Coefficients of determination for these three elements were relatively large. In the case of F, for example, 56 percent of the total variability observed among samples along this transect is attributed to distance from the powerplant. Severson and Gough (1976) arbitrarily used a coefficient of determination value of 0.50 in identifying the important proportion of the total variance attributable to the independent variable distance. The concentration of Ca in P. chlorochroa may also be related to operations at the powerplant, however, the slope of the regression line was significant only at a probability level of 0.10. Calcium also possessed a low coefficient of determination (table 4).

Ash yield, expressed as a percent of the dry weight of the lichen, showed a significant negative regression slope. This trend, along with the significant trends for F, Se, and Sr, is presented in figure 4. Since Ca, which is the major element in  $\underline{P}$ .  $\underline{chlorochroa}$  and  $\underline{comprises}$  between 12 and 33 percent of the  $\underline{ash}$  was most abundant in those samples

Table 4. -- Regression statistics for those elements and ash in Parmelia chlorochroa found to be

related to operations at the Dave Johnston powerplant

[All values are for the east transect; significance of the slope is the probability level at which the slope is different from zero; number of samples equaled 12 in whereas calcium and strontium were determined on the ash material; D= distance] all instances; ash, fluorine, and selenium were determined on the dry material

Element or ash	Regression equation	Significance of slope	Coefficient of determination	Observed range
Ash, %	$Log_{10}$ ash = 1.38 - 0.23 $log_{10}$ D	< 0.01½/	0.58	7.5-22
Calcium, %	Log Ca = 1.50 - 0.06 log D	.10	.25	20-33
Fluorine, 7	Log <sub>10</sub> F =-2.22 - 0.24 log <sub>10</sub> D	<b>.</b> 01	• 56	0.0020-0.0050
Selenium, ppm	$Log_{10}$ Se = 0.21 - 0.30 $log_{10}$ D	• 01	09.	0.35-1.40
Strontium, ppm	$Log_{10} Sr = 2.90 - 0.32 log_{10} D$	.01	.55	200-700

1/ The relation may be fortuitous. See discussion in text.

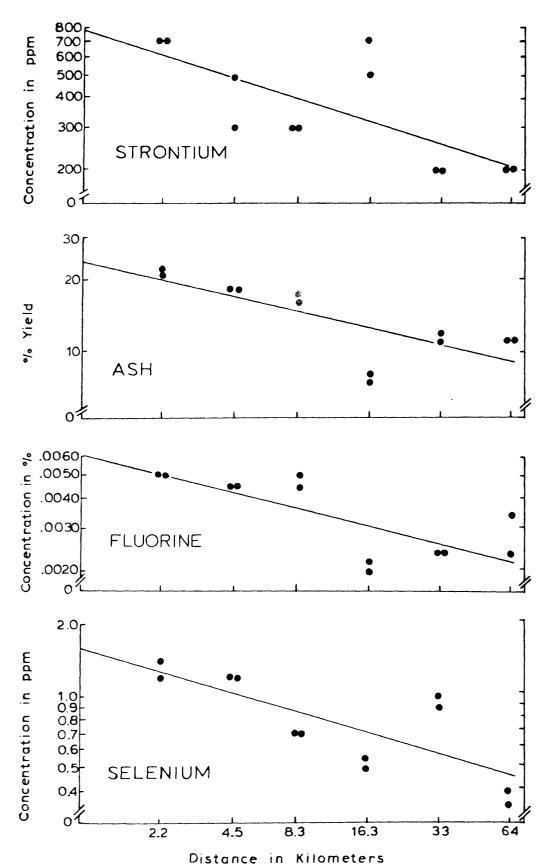


Figure 4.--Regression trends in <u>Parmelia chlorochroa</u> for concentrations of fluorine, selenium, strontium, and ash progressing east from the Dave Johnston Powerplant. Slopes are significantly different from zero at the 0.01 probability level.

yielding high ash values and because Ca displayed a possible regression trend of importance, it appeared that this element might be responsible for the concurrent ash trend. A product-moment correlation analysis between Ca and ash, however, did not show a strong positive relation. This is evident from Appendix V, table 2, where it can be noted that the samples with the lowest ash values also had some of the highest (31 percent) Ca values.

Silicon, another major constituent of  $\underline{P}$ .  $\underline{chlorochroa}$  comprising between 8 and 18 percent of the ash, was also considered a possible cause of the ash trend. Silicon does not, however, decrease in concentration with increasing distance. Further, the correlation coefficient for the relation between Si and ash was not significant at the 0.05 probability level.

The intensity of selected calcite and quartz peaks on X-ray diffractograms of the ash of one sample at each sampling site downwind was measured. The ratio of the intensity of the calcite to quartz peaks was plotted against the percent ash of the samples. These data (fig. 5) show that, in general, the amount of calcite in the samples decreases relative to the amount of quartz as ash increases. This trend suggests that, even though the samples were washed, they were contaminated with soil-derived quartz. There is an exception in the sample with the highest ash yield in which very high calcite to quartz ratios were found. This indicates to us that this sample was both very "clean" (free of quartz) and high in Ca.

Variable ash is probably due to both intrinsically high or low Ca and to the relative contamination of the samples. The significant inverse trend observed between ash yield and distance from the powerplant might, therefore, be fortuitous and not related to the powerplant emissions but to a combination of variable Ca and Si contents and varying degrees of quartz contamination.

Inverse concentration-to-distance trends observed along the west transect were not subjected to regression analysis because of the small number of sample sites. Inspection of these data (Appendix V, table 2) indicates that Ca and Sr may reflect some influence from the operations at the powerplant whereas Se shows a very strong probable relation. Fluorine shows no apparent trend; however, the high values obtained correspond well with the high values observed for close-in samples along the east transect. The ash values show no trend adding support to the probability that the ash trend observed along the east transect is fortuitous.

Of the suspected contaminant elements and ash, only the Se values can be considered to be unusually high in P. chlorochroa relative to background levels (U.S. Geological Survey, 1975, p. 13), and then only in samples collected within 8 km from the powerplant (fig. 4). Although selenium is noted, in the 1975 report, to be highly variable among samples

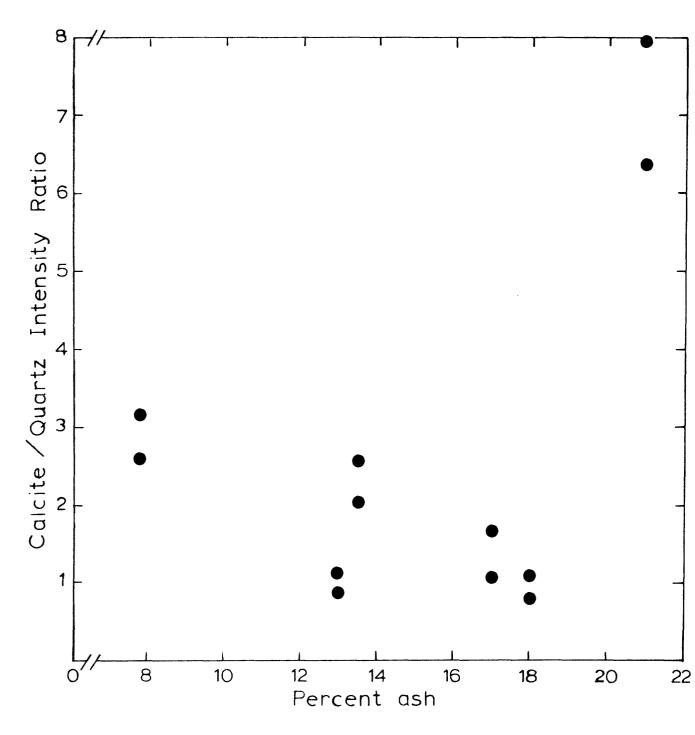


Figure 5.--Calcite to quartz x-ray diffraction peak intensity ratios from Parmelia chlorochroa ash plotted against percent ash yield.

of  $\underline{P}$ . chlorochroa collected from various parts of the basin, the maximum concentration noted in this study (1.20 ppm) is considerably above the observed range of values (0.20-0.70 ppm) for all samples in the 1975 basin-wide study.

It is of interest that in the study by Connor, Keith, and Anderson (1976), also at the Dave Johnston Powerplant, big sagebrush (Artemisia tridentata) samples, like the P. chlorochroa samples, showed significant regression trends for Se and Sr. Big sagebrush also showed significant regression trends for U and V whereas P. chlorochroa did not. Further, P. chlorochroa showed a trend for F whereas sagebrush did not. These findings lead to the following conclusions: (A) several elements tend to have higher concentrations in vegetation near the powerplant; (B) the most probable source of these accumulated elements is the powerplant; (C) differences in the metabolism, growth form, habitat, and microenvironment of different plant species result in differences in their accumulation of elements.

The use of cryptogams, and particularly lichens, as air pollution monitors has received considerable attention over the past decade (see, for example, Ferry, Baddeley, and Hawksworth, 1973). This present study indicates that the widespread terricolous lichen <u>P. chlorochroa</u> has potential use as a monitor of powerplant element emissions in the Northern Great Plains.

# CHEMISTRY OF POWDER RIVER SEDIMENTS by John R. Keith, Barbara M. Anderson, James M. McNeal and Josephine G. Boerngen

As part of a general effort to chemically characterize the landscape of the Powder River Basin, samples of Powder River stream sediments
were collected in 1973 according to a nested analysis of variance design.
The length of the river across the basin was subdivided into six segments,
each defined as that length of stream course which occurs in a "supertownship" of Connor, Keith, and Anderson (1976) as shown in figure 6.
In each segment, two localities were selected randomly, each locality
being about the size of a section (1.6 km on a side). The objective was
to reach the river somewhere within each locality and randomly collect
two samples of the "active" sediment from a transect across the river
bottom. In practice, the transect reached only to the edge of running
water, on the side from which the river was approached. The levels in
this design reflect geochemical variation 1) between supertownships, 2)
between transects within supertownships, 3) between samples within
transects, and 4) between analyses of sample splits.

In general, the two samples from each transect were located about 25-100 m apart. Each was collected by shovel, placed in a cloth bag, brought to the laboratory and, if necessary, dried before processing. Each sample was disaggregated and passed through a 2-mm sieve. The <2 mm fraction was further sieved into four size fractions-->200  $\mu$ m, 100-200  $\mu$ m, 63-100  $\mu$ m, and <63  $\mu$ m, which are denoted as the A, B, C and D size fractions, respectively. Fifteen of the resulting 96 samples were randomly selected and split into two parts and the entire suite of 111 samples was submitted for analysis in a randomized sequence. The analytical procedures used are described in Miesch (1976). Due to inadequate amounts in some of the size fractions, some chemical constituents could not be determined in all samples. The analysts are J. G. Crock, I. C. Frost, J. Gardner, W. Mountjoy, V. E. Shaw, and J. A. Thomas.

The analysis of variance results are shown in table 5. Except for  ${\rm Na_2O}$ , Ti, and Zr, which show significant components for three of the four size fractions, the listed constituents show little important large-scale variability. Thus, for many of these properties, provisional baselines may be estimated which should adequately represent a regional background for the length of the river in the basin.

Most broad-scale elemental variation appears in the coarser fraction (A) of these sediments. Thirteen entries in table 5 show such significant variation, including K, Li,  $Na_2O$ , and MgO which may reflect variation in feldspar content or exchangeable ion capacity clay aggregates, or both. Large-scale variation in Ti and Zr in the C and D (finest) fractions as well as in the A fraction probably indicates downstream variation in heavy mineral content. The fraction showing the least broad-scale (downstream) geochemical variability for most elements is the B-fraction,

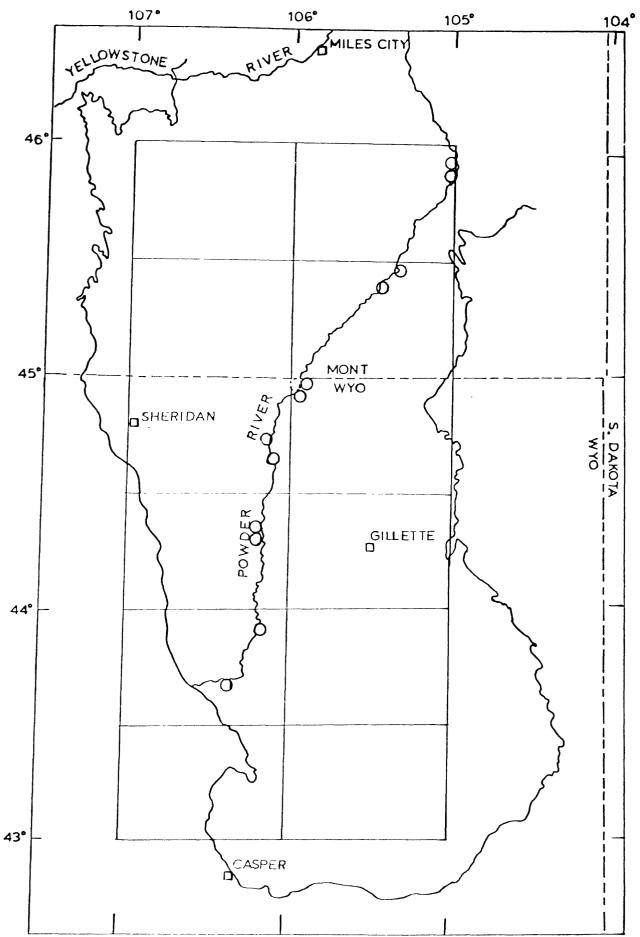


Figure 6.--Powder River Basin, with sampling localities (circles) of Powder River stream sediments. Rectangles are "supertownships" of Connor, Keith, and Anderson (1976).

although the environmentally important element Hg does vary significantly at this scale in this fraction. Thus, for a large variety of trace elements (B, Ba, Co, Cu, Li, Nb, Ni, Pb, Rb, Sr, V, Y, Rb, Zn and Zr) the B-fraction of these sediments constitutes the most geochemically uniform stream "monitor".

There is a tendency for the elements to have higher concentrations in the finer fractions. This is best seen in the geometric means in table 5; average concentrations in fraction D are particularly high. This may reflect the fact that the most common constituent, in the larger-grain-size fractions, is quartz which serves to dilute other constituents. Also, there is a tendency for a decrease in variation with decreasing grain size as shown by the geometric deviations in table 5. The combination of increasing concentration and decreasing variance with smaller-grain size indicates that the finer-sized fraction of these sediments is the more easily characterized in a chemical sense. This is so because a smaller variance requires fewer samples for a stable estimate of a mean, and a higher-mean concentration increases chances of detecting the constituent.

Finally, a preliminary 2-way analysis of variance test (supertownships vs. size fractions) suggests that no significant interaction is present except for Ti, Y, Yb and Zr. Again these metals are expected to occur largely in the heavy mineral fraction. This suggests that not only does the heavy mineral component vary significantly along the stream course, but its variation is somewhat dependent on grain size as well.

Table 5.--Statistical analysis of partial chemistry of the Powder River stream sediments

ΓA, 2 mm-200u fraction; B, 100-200µ fraction; C, 63-100µ; D, <63µ fraction; \*, statistically significant from zero at the 0.05 probability level. Data are in parts per million except where noted as percent; lendera (---) indicate insufficient data for baseline estimation. Ratio gives the number of samples in which constituent was determined to total number of aamples analyzed]

1			Varian	ice componer	it, percen	t			Summary a	tatistics	
Constituent	Size fraction	Total Log <sub>lo</sub> variance	Between super- townships	Between transects	Between samples	Between analyses	Ratio	Geometric mean	Geometric deviation	Geometric error	Expected 95 percent range (Baseline)
Total C, Z	A	0.1173	19.6	21.3	47.6	11.4	23.24	0.77	2.20	1.31	0.16-3.73
	В	.0715	30.3	3.8	47.1	18.8	24: 24	.54	1.85	1.31	.16-1.85
	С	.0154	44.6	2.1	0	53.4	24: 24	.72	1.33	1.23	.41-1.27
	D	.0105	4.5	0	95.5	0	24: 24	1.22	1.27	< 1.02	.76-1.97
нв	- А	.3827	0	42.0	55.7	2.3	17: 24	.041	4.16	1.24	.002710
	В	.0688	26.3*	0	60.9	12.8	24: 24	.019	1.83	1.24	*
	С	.0612	0	0	85.6	14.4	24:24	.019	1.77	1.24	.006060
	D	.0230	14.2	0	47.6	38.2	24: 24	.030	1.42	1.24	.015060
Li	- A	.0966	28.8*	35.6	27.4	8.2	18: 24	12.	2.05	1.23	******
	В	.0292	21.1	0	51.8	27.1	24: 24	11.	1.48	1.23	5-24
	С	.0174	8.9	0	45.5	45.6	24: 24	12.	1.35	1.23	7-22
	D	.0094	13,8	0	1.7	84.5	24: 24	18.	1.25	1.23	12-28
MgO, 7	- A	.1607	31.2*	37.5	28.2	3.2	18: 24	.61	2.52	1.18	******
	В	.0319	35.4*	0	61.5	3.1	24: 24	.60	1.51	1.08	
	С	.0073	17.4	29.0	45.1	8.5	24: 24	1.07	1.22	1.06	.72-1.59
	D	.0012	0	5.1	83.4	11.5	24: 24	1.83	1.08	1.03	1.57-2.13
Na <sub>2</sub> 0, %	- А	.0048	58.2*	0	36.8	5.0	18: 24	.95	1.17	1.04	
	В	.0050	0	49.8	25.2	25.0	24: 24	.72	1.18	1.08	.52-1.00
	С	.0018	49.7*	17.1	33.2	0	24: 24	.80	1.10	< 1.01	
	D	.0013	43.3*	0	56.7	0	24:24	.84	1.09	< 1.01	*******
Rb	- А	.0161	4.7	40.4	28.3	26.6	18: 24	60.	1.34	1.16	33-108
	В	.0176	24.2	11.6	39.9	24.3	24: 24	49.	1.36	1.16	26-91
	С	.0161	36.9*	0	36.5	26.6	24: 24	53.	1.36	1.16	
	D	.0105	0	0	59.6	40.4	24: 24	61.	1.27	1,16	38-98
Zn	- А	.0538	20.9.	56.9 <del>*</del>	10.3	11.9	18: 24	46.	1.71	1.20	16-135
	В	.0215	6.9	2.6	60.7	29.9	24: 24	35.	1.40	1.20	18-69
	С	.0103	7.7	0	29.8	62.5	24: 24	38.	1.26	1.20	24-60
	D	.0066	0	24.6	60.0	15.4	24: 24	67.	1.21	1.08	46-98

Table 5.--Statistical analysis of partial chemistry of the Powder River stream sediments -- Continued.

			Varian	ce componen	t, percen	t			Summary s	tatistics	
Constituent	Size fraction	Total Log <sub>10</sub> variance	Between super- townships	Between transects	Between samples	Between analyses	Ratio	Geometric mean	Geometric deviation	Geometric error	Expected 95 percent range (Baseline)
A1, %	A	0.0642	< 0.1	52.7*	30,5	16.8	23; 24	.4.88	1.79	1.27	1.7-14
	В	.0232	< .1	< .1	64.6	35.4	24; 24	3.57	1.42	1.23	2.0-6.2
	С	.0331	21.4	< ,1	41.5	37.1	24: 24	4.01	1,52	1.29	2.1-7.7
	D	.0162	29.1*	< .1	54.4	16.4	23: 24	6,12	1.34	1.13	
В	A	.0364	17.4	42.8	< .1	39.8	13:24	14	1.55	1.32	7.0-28
	В	.0192	7.7	< ,1	< .1	92.3	13: 24	14	1.38	1.36	12-17
	С	.0518	8.6	< .1	< .1	91.4	24: 24	32	1.69	1.65	23-44
	D	.0212	< .1	34.8	40,1	25.2	24: 24	55	1.40	1.18	31-99
Ва	A	.0205	< .1	67.9*	< ,1	32.1	24: 24	870	1.39	1.21	510-1,500
	В	.0280	4.3	24.3	21.8	49.7	24: 24	870	1.47	1.31	510-1,500
	С	.0179	26.5	< .1	73.5*	< .1	24: 24	930	1.36	< 1.02	500-1,700
	D ´	.0255	34.6*	< ,1	< .1	65.4	24: 24	1,030	1.44	1.35	******
Be	D	.0299	14.6	< .1	16.6	68.9	17: 24	1	1.49	1.39	.64-1.6
Ca, %	A	.0791	5.0	40.5*	< .1	54.4	24: 24	2.02	1.91	1.61	.84-4.9
	B	.1025	15.6	< .1	84.4	< .1	24: 24	1.13	2.09	< 1.02	.26-4.9
	C	.0168	21.2	< .1	78.8*	< .1	24: 24	1.85	1.35	< 1.02	1.0-3.4
	D	.0247	< .1	< .1	84.3*	15.7	24: 24	3.18	1.44	1.15	1.6-6.1
Co	٨	.0500	6.3	30.4	10.7	52.6	24: 24	6	1.67	1.45	2.9-12
	В	.0306	14.0	23.6	8.7	53.7	23: 24	4	1,50	1.34	2.3-7.0
	С	.0172	1.4	29.4	24.2	45.0	24: 24	3	1.35	1.22	1.9-4.7
	D	.0117	< .1	29.2	48.1	22.8	24: 24	6	1.28	1.13	3.9-9.2
Cr	A	.1705	14.4*	33.2	6.9	45:5	24: 24	26	2.59	1.90	
	В	.1060	19.4*	< .1	75.7*	4.9	24: 24	18	2.12	1.18	
	С	.0587	7.6	14.6	71.1	6.6	24: 24	31	1.75	1.15	11-91
	D	.0574	34.5	26.4*	28.4	10.7	24: 24	79	1.74	1.20	28-220
Cu	A	.1856	33.3*	3.2	< .1	63.5	24: 24	18	2.70	2.20	
	В	.0858	1.7	< .1	90.0*	8.3	24: 24	. 9	1.96	1.21	2.5-33
	С	.0250	19.1	< ,1	49.9	31.0	24: 24	10	1.44	1.22	5.5-18
	D	.1664	< .1	< .1	97.7*	2.3	24: 24	34	2.56	1.15	5.3-220

Table 5.--Statistical analysis of partial chemistry of the Powder River stream sediments -- Continued.

			Varian	ice componen	t, percen	t			Summary s	tatistics	
<b>Consti</b> tuent	Siza fraction	Total Log <sub>10</sub> variance	Between super- townships	Between transects	Between samples	Between analyses	Ratio	Geometric mean	Geometric deviation	Geometric error	Expected 95 percent range (Baseline)
Fe, %	٨	0.0665	<0.1	57.0*	1,3	41.7	24: 24	2.88	1.81	1.47	1.2-7.1
	В	.0301	< .1	4.2	70.0	25.8	24: 24	1.52	1.49	1.22	.76-3.0
	С	.0151	5.2	< .1	68.9	25.9	24; 24	1.67	1.33	1.15	1.0-2.7
	D	.0194	< .1	10.6	49.4	40.0	24: 24	2.58	1.38	1.22	1.6-4.2
Ga	A	.0496	20.8*	19.1	27.3	32,8	24; 24	13	1.67	1.34	
	В	.0248	19.2	< .1	64.7	16.1	24: 24	10	1.44	1.16	5.2-19
	С	.0185	12.4	< .1	55.3	32,4	24: 24	10	1.37	1.20	6.01-17
	D	.0076	8.7	22.8	68.5*	< .1	24: 24	15	1.22	< 1.02	10-22
K, %	A	.0172	15.6*	25.9	4.7	53.8	24; 24	2.90	1.35	1.25	
	В	.0106	10.0	< .1	41.0	49.0	24: 24	2.11	1.27	1.18	1.5-2.9
	C	.0063	16.2	< .1	22.2	61.6	24: 24	2.11	1.20	1.15	1.7-2.6
	D	.0146	< .1	20.4	< .1	79.6	24: 24	2.68	1.32	1.28	2.1-3.4
La	D	.0683	37.2*	< .1	19.2	43.7	23; 24	49	1.83	1.49	
Mn	A	.0446	< .1	29.7	< .1	70.3	24: 24	310	1.63	1.50	180-520
	В	.0198	< .1	55.2*	31.6	13,1	24: 24	220	1.38	1.12	120-400
	С	.0147	< .1	17.8	82.2*	< .1	24: 24	220	1.32	< 1.01	130-380
	D	.0301	37.6*	11.3	38.2	12.9	24: 24	300	1.49	1.15	
иь	В	.0247	< .1	< .1	24.5	75.5	13: 24	6	1.44	1.37	4.2-8.6
	C	.0282	38.4*	< .1	61.6*	< .1	20: 24	10	1.47	< 1.01	
	D	.0241	20.7	< .1	< .1	79.3	24: 24	14	1.43	1.37	10-19
N1	A	.1059	32.6*	< .1	17.8	49.6	24: 24	13	2.12	1.70	
	В	.0443	21.5	< .1	43,9	34.6	24: 24	6	1.62	1.33	5.2-13
	c	.0257	25.4	3.3	< .1	71.3	24: 24	6	1.45	1.37	4.0-8.9
	D	.0230	< .1	17.0	< .1	83.0	24: 24	13	1.42	1.37	9.8-17
Pb	A	.0115	5.8	60.4*	< .1	33.9	24: 24	17	1.28	1.15	
	В	.0101	13.2	< .1	7.8	79.1	24: 24	11	1.26	1,23	8.9-14
	С	.0084	7.4	< .1	< .1	92.6	24: 24	11	1.23	1.23	9.8-12
	D	.0078	< .1	< .1	< .1	100	24: 24	16	1,23	1.23	

Table 5.--Statistical analysis of partial chemistry of the Powder River stream sediments -- Continued.

			Varian	ice componen	it, percen	t			Summary s	tatistics	
Constituent	Size fraction	Total Log <sub>10</sub> variance	Between super- townships	Between transects	Between samples	Between analyses	Ratio	Geometric mean	Geometric deviation	Geometric error	Expected 95 percent range (Baseline)
Sc	Α	0.1275	15.5	10.6	48.1	25.8	15: 24	3	2.28	1.52	2.7-3.4
	С	.0365	< .1	39.6	39.2	21.2	20: 24	3	1.55	1.22	1.4-6.6
	D	.0294	28.7*	< .1	11.4	59.9	24: 24	6	1.48	1.36	
Sr	A	.0320	13.1	44.4	9.4	35.1	24: 24	180	1.51	1.27	92-350
	В	.0144	1.9	23.5	3.0	71.6	24; 24	130	1.32	1.26	97-170
	c	.0124	50.4*	< .1	49.6*	< .1	24: 24	140	1.29	< 1.01	
	D	.0087	6.6	< .1	48.7	44.6	24: 24	180	1.24	1.15	130-250
Ti, %	A	.1132	25.2*	11.7	4.3	58.8	24: 24	.090	2.17	1.81	
	В	.0351	< .1	45.6*	< .1	54.4	24: 24	.10	1.54	1.37	.05618
	c	.0355	36.6*	14.4	49.0*	< .1	24: 24	.17	1.54	< 1.01	
	D	.0341	36.1*	< .1	63.9*	< .1	24: 24	.32	1.53	< 1.01	
v	A	.1383	30.9*	15.1	25.7	28.3	24: 24	52	2.35	1.58	
	В	.0386	< .1	7.6	79.0	13.4	24: 24	37	1.57	1.18	16-85
	С	.0226	27.2	< .1	18.4	54.4	24: 24	54	1.41	1.29	34-86
	D	.0268	11.5	< .1	54.9	33.6	<b>2</b> 4: 24	92	1.46	1.24	50-170
γ	A	.0374	40.1*	3.7	18.7	37.5	24: 24	18	1,56	1.31	
	В	.2326	15.4	< .1	84.6*	< .1	24: 24	13	3.04	< 1.01	
	С	.0230	21.6	< .1	27.8	50.6	24: 24	19	1.42	1.28	12-31
	D	.0501	38.6*	19.6	9.5	32.3	24: 24	48	1.67	1.34	****
Yb	A	.0341	34.4*	23.6	4.6	37.4	24: 24	2	1.53	1.30	*****
	В	.0262	12.3	< .1	68.0	19.7	24: 24	2	1.45	1.18	1.0-3.9
	С	.0350	41.8*	< .1	58.2*	< .1	24: 24	2	1.54	< 1.01	*****
	D	<b>.0</b> 603	48.7	7.9	18.6	24.8	24: 24	6	1.76	1.33	2.3-16
Zr	A	.0404	32.3*	12.3	35.6	19.8	<b>2</b> 4: 24	61	1.59	1.23	****
	В	.0231	1.6	< .1	50.3	48,1	24: 24	76	1.42	1.27	46-130
	С	.1123	49.6*	< .1	30.2	20.2	24: 24	210	2.16	1.41	
	D	.1890	31.7*	9.9	56.4*	2.0	24:24	820	2.72	1.15	

# SOIL AND SAGEBRUSH CHEMISTRY NEAR THE JIM BRIDGER POWERPLANT by Barbara M. Anderson and John R. Keith

#### Introduction

A study of big sagebrush (<u>Artemisia tridentata</u> Nutt.), surface soils (0-2.5 cm in depth), and subsurface soils (5-20 cm in depth) along four traverses radiating away from the Jim Bridger Powerplant, Sweetwater County, Wyoming, was started in August, 1973. By sampling before the powerplant was fully operational, it was intended that the geochemical background could be established along these traverses for future monitoring of possible trace-element changes. In general, many element concentrations vary widely along these traverses and some show systematic increases or decreases outward from the powerplant. Many of these decreases can be explained as expected geochemical changes in the substrate.

The Jim Bridger Powerplant of the Pacific Power and Light and Idaho Power Companies is located 56 km northeast of Rock Springs, Wyoming, near Point of Rocks. At full capacity in 1978, the plant will be one of Wyoming's largest coal-fired powerplants, and will consist of four stacks, each fifty stories tall, with a rated capacity of 500 MW(e) per unit, adding two million kilowatts of power to the Wyoming-Idaho and Pacific Northwest grid. Construction was started in 1971, with the first unit becoming operational in the winter of 1974.

The Jim Bridger Powerplant uses subbituminous coal from the Fort Union Formation. At full capacity, the plant will consume 14.4 metric tons a minute over its expected life of 35 years. The coal will come from a strip mine located east of the powerplant that is owned by Union Pacific and the Federal government. Water for the plant is supplied by a 64-km pipeline from the Green River (Strabala, 1974).

### Physiographic setting

The Jim Bridger Powerplant is located along the northeast flank of the Rock Springs Uplift, an elongated anticline with a north-trending axis, and sits on the Cretaceous Almond Formation near its contract with the Lewis Shale Formation. The non-marine Almond Formation consists of sandstone, siltstone, carbonaceous shale, and minor coal beds. The marine Lewis Shale is composed of light-to-dark gray calcareous to non-calcareous shale and fine-grained sandstone (Spitzer and May, 1975). All bedrock in the area of study consists of sedimentary rocks of upper Cretaceous and lower Tertiary age that crop out in high-walled rock faces or escarpments.

The climate of the area is that of a Middle Latitude Steepe (Trewartha, 1954), where potential evapotransipiration from the soil and vegetation generally exceeds the average annual precipitation. The average temperature of the coldest months is below freezing. The precipitation ranges from 15-38 cm/year, most falling as snow in the winter. Winds are predominantly out of the west and southwest.

The soils of this area are derived primarily from shales and tend to be high in soluble salts and low in nitrogen. The soils, in general, are considered to be warm and dry and lack moisture for plant growth for long periods. The most common soils in the area are classified as Haplargid plus Torriorthents (U.S. Geological Survey, 1970). They are light brown, have a loamy horizon of clay accumulation, are low in organic matter, and are rarely moist for more than three consecutive months. Salorthid soils are also present and are characterized by no horizon or accumulation of clay, but may have accumulations of calcium carbonate, gypsum, or other salts.

The vegetation of the Jim Bridger area is a sagebrush steepe (Küchler, 1964), consisting of open grassland with dense to open shrub stands. The dominant grass is bluebunch wheatgrass (Agropyron spicatum (Pursh) S. and S.). Growing throughout the area is a number of species of sagebrush, but only the dominant species, big sagebrush (Artemisia tridentata Nutt.), was chosen for the botanical part of this study.

#### Methods of sample collection and preparation

All samples of sagebrush and soils were collected in August 1974. Plant samples were collected using stainless steel shears. Each plant sample (approximately 50 g) consisted of stems and leaves from the terminal 15 cm. The samples were stored in quart-size, refrigerator-freezer boxes. In the laboratory, the unwashed plant tissue was ashed and analyzed for a variety of metals using emission spectrographic, atomic absorption, selective ion electrode, and other techniques described in U.S. Geological Survey (1975, p. 74-78) and Miesch (1976, p. 14). The elements fluorine, total sulfur, arsenic, mercury, and selenium were determined in dry plant material.

The soil samples were collected by first removing coarse surface material and plant or other non-soil debris. At all sites, a surface soil sample (0-2.5 cm depth) and a subsurface soil sample (5-20 cm depth) were collected using a chrome-plated trowel. The samples (approximately 200 g each) were stored in paper soil envelopes and were analyzed by methods described in Miesch (1976).

All plant and soil samples were analyzed in a randomized sequence to reduce possible effects from systematic laboratory error. The samples were prepared and analyzed in laboratories of the U.S. Geological Survey in Denver. Analyses were performed by J. Baker, L. Bradley, W. Cary, C. Freeman, J. Gardner, P. Guest, T. Harms, R. Havens, C. Huffman, Jr., L. Lee, V. Merritt, C. Papp, L. Riley, V. Shaw, G. Shipley, J. Thomas, R. Van Loenen, J. Wahlberg, and T. Yager.

### Sampling Design

The sampling design consisted of collecting soil and plants at geometrically increasing distances along four traverses radiating north, east, south, and west from the powerplant (fig. 7). At each locality two sites, separated by about 230 m, were chosen. A sample each of big sagebrush, surface soil, and subsurface soil was collected at each site. Five localities were sampled along both the north and south traverses, and six localities were sampled along the east and west traverses. There were a total of 22 sampling localities from which 44 sagebrush samples and 84 soil samples were collected (no soils were collected at site 3E). Analytical results and distances of samples from the powerplant are given in Appendix V, table 3.

### Statistical analysis and results

Connor, Keith and Anderson (1976) successfully used a log-linear function of the following form to relate metal concentration in the landscape to distance from the Dave Johnston Powerplant:

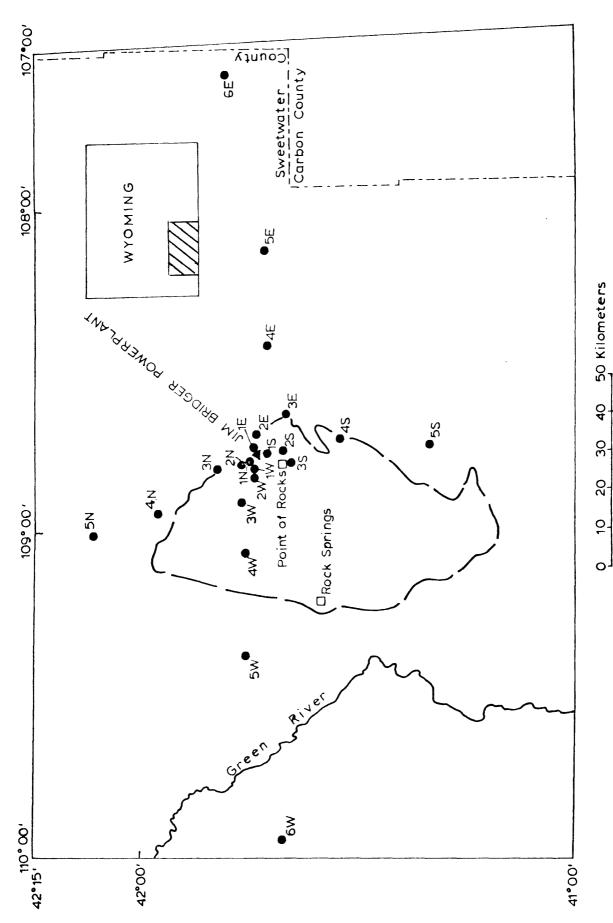
$$Log X = a + b (Log D)$$

Log X is an estimate of the logarithmic concentration of a chemical constituent at a point and Log D is the logarithm of the distance in kilometers of the point from the powerplant. The coefficient, a, is the estimated logarithmic concentration at  $1\ km$  and the coefficient, b, is the estimated slope of the concentration trend away from the powerplant.

Because one effect of element emissions from a powerplant is assumed to be a continual element accumulation in the landscape near the powerplant, the logarithmic model given above should have a negative b coefficient if such accumulation is pronounced enough.

Inasmuch as the work described here was undertaken prior to completion of the Jim Bridger generating plant, it was not expected that geochemical variation related to the logarithm of distance from the powerplant would be found in either soils or sagebrush; that is, b was expected to be near zero. However, a large number of significant relations were found in this study, particularly along the southern traverse (table 6). Thirteen chemical constituents along this traverse significantly increase with distance in both the surface and subsurface soils, including  $Al_2O_3$ , the most important constituent of clay (Appendix V, table 3). In addition,  $SiO_2$  in the subsurface decreases in a significant way. Clearly, these changes reflect, in large part, lithic changes in bedrock from dominantly shale of Cretaceous age at localities 1S, 2S, and 3S to dominantly sandstone of Tertiary age at localities 4S and 5S.

Increases in elemental concentration away from the powerplant were also found to be significant for a number of constituents along the west traverse, although here the dominant effect appears to be noticeably low concentrations in localities 1W and 3W (Appendix V, table 3). The



Powerplant (solid triangle), Wyoming. Approximate position of the Upper Cretaceous-Lower Tertiary contact is shown by long-dashed line. Figure 7. -- Soil and sagebrush sampling localities (solid dots) for four traverses from the Jim Bridger

Table 6.--Percent of total observed logarithmic variation in sagebrush and soil constituents accounted for in terms of logarithmic distance from the Jim Bridger Powerplant.

[A, sagebrush ash; S, surface soil (0-2.5 cm depth); SS, subsurface soil (5-20 cm depth); percentage in parentheses indicates an increase in concentration with distance, otherwise percentage indicates a decrease in concentration with distance; blank, distance-related variation is not significant at the 0.05 probability level]

				Dir	ection	of sa	mplin;	g trav	erse			·
		North			East			South			West	-1
Constituent	A	S	SS	A	S	ss	A	S	ss	A	S	ss
Fe	62							(77)	(71)			
Ca							41				(34)	(34)
Ti	58							(69)	(51)			
Mn								(91)	(78)			
В		46			48		42					
Co								(78)	(58)		(45)	
Cr								(81)	(65)		(33)	
Cu								(74)	(53)			
Ni	50								(62)			
Pb								(40)			(69)	
Sc								(78)	(78)		(39)	(48)
Sr								(47)		(54)	(46)	(36)
v								(65)	<b>(7</b> 0)		(33)	(31)
Y			57					(69)	(44)			
Zr		(45)	(57)					(68)	(51)			
P										38		
Ga								(63)	(89)			
Li		(37)						(74)				
MgO						47		(68)	(59)			(38)
Na <sub>2</sub> O		(84)	(89)		(73)	(62)						
F	47 <u>1</u>	/										
C, total		37			51	65						
C, carbonate					44	44					(35)	(37)
C, organic			41		45				(51)			
A1203								(76)	(83)			
S102									53			45
Se	60 <u>1</u>	/										
Ash	491	/										
Cd							(78)					
Si	42											

<sup>1/ (</sup>enstituent determined on dry weight.

importance of the major element, Ca, here suggests, again, a geologic control. These two sites are relatively low in Ca (and in the subsurface are relatively high in  $\mathrm{SiO}_2$ ) and likely reflect a calcium-poor substrate. The increase in  $\mathrm{Na}_2\mathrm{O}$  along the north and east traverses may reflect a relatively high content of Na-Feldspar in the Tertiary rocks at localities 4N, 5N, 4E, 5E, and 6E.

Chemical variability in soil along the north and east traverses is less marked than along the south and west traverses. Carbon decreases along both, and Na $_2$ O increases along both suggesting, again, parental control of soil composition. In both directions, the parent bedrock changes from carbonaceous shale (relatively high carbon) to arkosic sandstone (relatively high Na $_2$ O). Controlling features of the trends in subsurface soil along the eastern traverse are the occurrence of high Na $_2$ O and Al $_2$ O $_3$ , and low MgO, and C (both total and organic) in localities 5E and 6E compared to the other localities. Similarly, total carbon in the surface soil, and yttrium and organic carbon in the subsurface soil of the northern traverse, and B in the surface of the eastern traverse largely reflect the occurrence of exceptionally high concentrations in samples closest to the powerplant (lN and lE). Possibly, such effects reflect construction or mining activities.

Regression analysis of the sagebrush chemistry resulted in many fewer significant relations than were found in the soils, and all but two of twelve trends so defined decrease away from the powerplant (figs. 8, 9 and 10). Of the four traverse directions, the one to the north exhibits the most trends (seven). Three of these trends (Fe, Ti, and F) are visibly controlled by high concentrations in the first locality, 1N (Appendix V, table 3), suggesting as mentioned above that they may be reflecting construction or mining activities. In this sense, the three elements can probably be viewed as point-source pollutants. Construction was heavy on the north side of the Bridger powerplant at the time of sampling, and the resultant suspended dust may have been a source of sagebrush contamination. This conjecture is supported by the higher ash and titantium values at localities close to the powerplant. According to Shacklette (1965), titanium is the most favorable trace metal in plant material for determining the extent of soil contamination. Unless the dust had a special character, it is difficult to account for the elevated fluorine. Nevertheless, its presence is especially interesting because this element seems to be an important pollution suspect in Vegetation at "on-line", coal-fired powerplants (this report, figs. 4 and 37).

Variation in Ca and B on the southern Traverse (fig. 10) is also largely controlled by elevated concentrations at the nearest site (1S). In contrast, the increase in Cd southward is strong, even if the first locality is ignored. Also, the trends in P (decreasing) and Sr (increasing) west of the plant are probably real but, again, lack a ready explanation. The positive slopes seen for Cd and Sr (fig. 10) are interesting because Cd is one of the more environmentally important

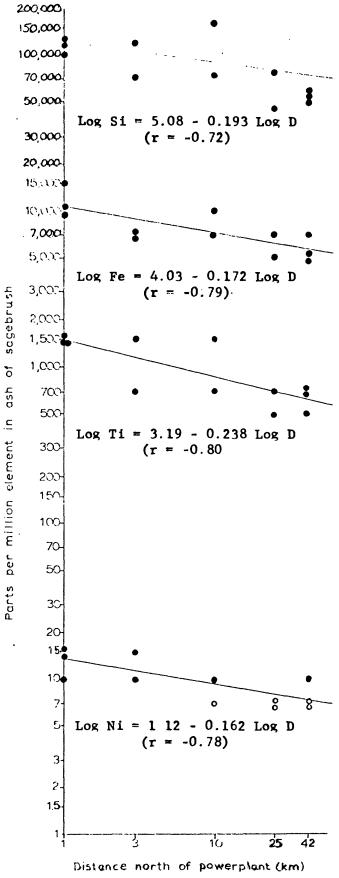
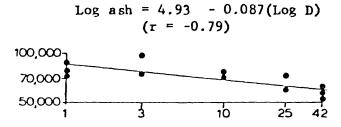


Figure 8.--Metal trends in ash of sagebrush north of the Jim Bridger Powerplant, Wyoming. Open circles indicate concentrations below the limit of analytical detection that are arbitrarily taken as about 0.7 of the limit. Correlation coefficients in parentheses Where three analyses are given at a site, two represent analyses of a single sample.



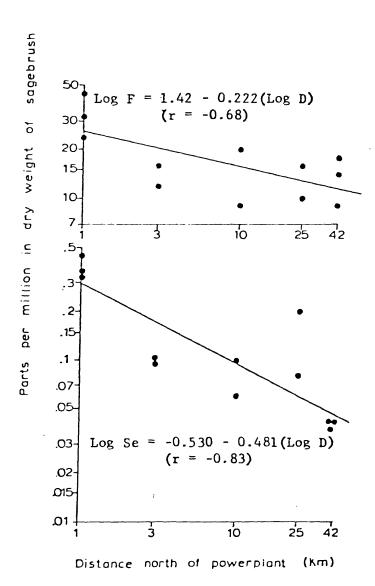


Figure 9.--Trends in dry weight of sagebrush north of the Jim Bridger Powerplant, Wyoming. Correlation coefficient in parenthesis. Where three analyses are given at a site, two represent analyses of a single sample.

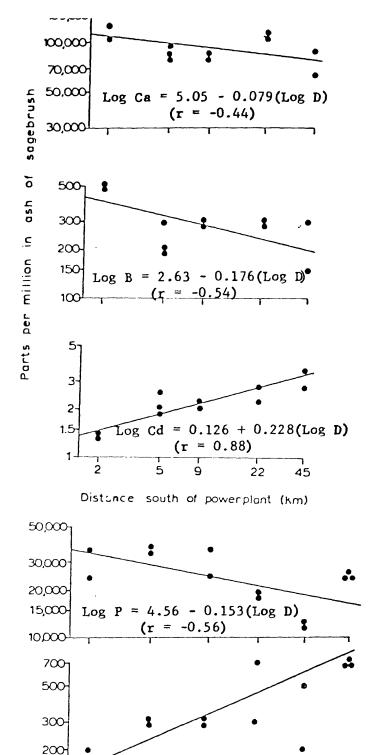


Figure 10.--Trends in ash of sagebrush south and west of the Jim Bridger Powerplant, Wyoming. Correlation coefficient in parenthesis. Where three analyses are given at a site, two represent analyses of a single sample.

Log Sr = 2.19 + 0.294(Log D)

Distance west of powerplant (km)

(r = 0.77)

elements, and Sr in big sagebrush is listed as a suspected pollutant around the Dave Johnston Powerplant (Connor, Keith, and Anderson, 1976). The low concentrations of both of these elements close to the powerplant indicate that if pollution "halos" were to develop in the future around this powerplant, they would not necessarily be exhibited by decreasing trends, at least along these particular traverses.

Metal trends in sagebrush involve a different and more limited suite of elements than do those of the soils, indicating that sagebrush geochemistry varies independently of substrate geochemistry. Moreover, if the sampling localities nearest the powerplant are ignored, six of the sagebrush trends (figs. 8, 9, and 10) would become either nonsignificant or strongly reduced. These observations suggest that a provisional estimate of the geochemical background in sagebrush is possible if summaries are based on all data except that from sites 1N, 1E, 1S, and 1W. Such summaries are given in table 7.

Table 7.--Geochemical summary of data from sagebrush (Artemisia

tridentata) around the Jim Bridger Powerplant, Wyoming

[Data in parts per million, except where noted as percent (%); GM, geometric mean; GD, geometric deviation; GE, geometric error; ratio gives the number of samples in which the constituent was determined to the total number of samples analyzed; leaders (--) indicate baseline cannot be estimated with given data]

	T				Expected 95 percent range
Constituent	Ratio	GM	GD	CE	(Bascline)
As1/ .	38: 41	0.15	2.46	1.22	0.026-0.87
<u>F1</u> /	41: 41	15	1.71	1.26	5.7-39
Hg1/	41: 41	.019	1.45	1.14	.0094038
S	41:41	.15	1.26	1.10	.09923
se <u>1</u> /	41:41	.15	2.59	1.10	.023-1.0
Ash, 21/	41:41	6.9	1.25	1.08	4.6-10
A1, %	41:41	2.2	1.62	1.17	.88-5.5
В	41:41	260	1.43	1.46	
Ва	41:41	310	1.64	1.17	120-790
Ca, %	41:41	9.1	1.24	1.04	5.9-14
Cd	41:41	2.8	1.72	1.15	.98-8.0
Co	41:41	1.8	1.93	1.40	.58-5.6
Cr	41:41	16	1.61	1.15	6.4-40
Cu	41:41	110	1.42	1.30	69-170
Fe, %	41:41	.68	1.64	1.29	.29-1.6
K, %	41:41	23	1,33	1.09	13-39
Li	41:41	13	1.59	1.19	5.5-31
Mg, 7	41:41	1.5	1.31	1.33	
Mn	41:41	470	1.53	1.37	270-830
Y.o	41:41	9.8	1.39	1.30	6.6-15
lia, Z	41:41	.21	1.83	1.22	.06766
κi	32:41	10	1.64	1.25	4.1-24
P, 7	41: 41	2.7	1.46	1.15	1.3-5.4
Pb .	41:41	46	1.53	1.38	26-80
£1, Z	41: 41	8.6	1.63	1.14	3.4-22
Sr.	41: 41	360	1.64	1.21	140-900
Ti	41:41	910	1.73	1.48	420-2,000
υ	40: 41	.77	1.57	1.21	.34-1.8
ν	40:41	26	1.85	1.33	8.8-77
Zn	41:41	280	1.55	1.10	120-660
Zr	41:41	59	1.71	1.30	23-150

 $<sup>\</sup>underline{1}$ / Determined on dry weight.

## GEOCHEMISTRY OF GREEN RIVER OIL SHALE by Walter E. Dean

#### Introduction

This report brings together a wide variety of selected trace and minor element data on the Green River oil shale in order to examine in a provisional way, the geochemical variability of those bedrock materials likely to be brought to the surface by energy-related activities. Table 8 summarizes data from six sources. General sample locations are shown in figure 11.

Included here are summaries based on unpublished as well as published work. A search was made of the U.S. Geological Survey's Rock Analysis Storage System (RASS) for analyses of oil shale from the Piceance Creek (Colorado), Uinta (Utah), and Green River (Wyoming) Basins. Where possible, only analyses of drill core samples were included in the compilation in order to eliminate possible weathering effects; however, all samples from the Green River Basin were collected from outcrops or roadcuts. The groups of RASS analyses are referenced by the name of the sample submitter, all of whom are Geological Survey personnel. Most of the analyses are of samples from potentially economic oil shale zones in the upper part of the Green River Formation. A few additional trace element data may be found in Stanfield and others (1951) and Smith and Stanfield (1964).

Seven trace elements listed in table 8 are generally considered of particular environmental interest, and geochemical work by the lessees in the prototype oil shale program has focused on analyses for these elements in both oil shale and soil as part of predevelopment baseline environmental assessments. These elements are cadmium, antimony, arsenic, mercury, selenium, fluorine, and boron. Ranges in concentration reported in table 8 for minor and trace elements are shown in figure 12. Also shown in figure 12 are provisional estimates of average concentrations.

The dominant minerals in Green River oil shale are quartz, dolomite, albite, and calcite (usually in that order of abundance) with minor amounts of siderite, analcime, K-feldspar, dawsonite, and nahcolite, all of which may occur locally as major constituents. Therefore, the dominant major elements are silicon (quartz + minor albite, analcime, and K-feldspar), aluminum (albite, dawsonite, and K-feldspar), and sodium (albite, dawsonite, and nahcolite). Iron usually occurs in concentrations between 1.5 and 2 percent, and is present mainly in pyrite, ferroan dolomite, and siderite. Titanium rarely occurs in concentrations greater than 0.2 percent, and minor amounts of phosphorus and sulfur are usually present, mainly in the form of apatite (phosphorus), and organic material and pyrite (sulfur). Desborough and others (1976) examined the mineralogy of oil shale by X-ray diffraction and attempted to relate element abundances to mineralogical residences. Additional reports on the mineralogy of the Green River oil shale include Smith (1974), Desborough and Pitman (1974), Robb and Smith (1974), Beard and others (1974), Dyni (1974), Desborough (1975), Desborough and Pitman (1975), Desborough (1976).

Table 8.--Ranges, geometric means (<u>OM</u>) and geometric deviations (<u>GD</u>) of concentrations of selected elements in Green River oil shale from the Piceance Creek (Golorado), Uinta (Utah), and Green River (Wyoming) Basins,

[Data in parts per million, except where noted as percent (7); leaders (--) indicate no data]

Green Fiver	Basin Vi∩e≟/		1	1	}	!	:	 	20-500 43 2,87		0.7-7.0 2.6 2.05	0.50-10 3.7 2.60
Vinta Basin	$Vine^{1/}$		<u> </u>	!	1	}	1		<20-100 38 2.00		0.7-5.0 2.1 2,15	0.70-3.0
T.	Desperougn et al. 1		<0.6-1.2	1-6 2.1	25-75 37	<0.08-2.9 0.35	<0.1 - 3 1.1 3	700-2,100 1,200	30-300 86		1.3-2.7	0.60-4.8
	Cook 6/	s	0.14	0.39	7.2	<0.1	0.08	1,700	140		ı	1
Basin	/5d-5	ant" elemonts	<pre>&lt;0.5-0.7 (all but 3 &lt;0.5)</pre>	<1 - 3 1.2 1.65	-10-125 38 1.90	<0.02-1.3 0.22 1.73	<pre>&lt;2 - 10 2.2 1.82</pre>	600-3,400 1,300 1.40	10-300 41 2.02	elements	:	1
Creek	C-a-/	ally import	0.54 - 4.0 2.4 1.22	0.10-2.8 0.49 1.67	0.90-15 6.5 1.64	0.05-3.6 0.60 1.91	0.10-1.3 0.32 1.91	75-1,500 550 1.64	1 – 516 129 1.79	Other e	ł	<b>!</b>
Piceance	Donnell $^{3}$	"Environmentally important"		!	!	0.10-1.5 0.44 2.34	1				i	!
	Dyni <sup>2</sup> /		1	1	!	!	<u> </u>	1	<20-500 22 3.00		0.3-5.0	0.30-5.0 2.3 1.88
	Vine <sup>1</sup> /		!	1	1	1	}	ļ	<30-300 58 1.87		1.2-2.8 1.9 1.27	0.10-7.0 2.1 3.55
	Element		Cadhilun range G.M.	Antimony range G.M. G.D.	Arsenic range G.M.	mercury range G.M.	range G.M.	ruorine range G.M.	range G.M.		Iron, % range G.M. G.D.	Magnesium, % range G.M. G.D.

Table 8.--Ranges, geometric means (GM) and geometric deviations (GD) of concentrations of selected elements in Green River oil shale from the Piceance Creek (Colorado), Uinta (Utah), and Green River (Woming) Basins -- Continued.

			Piceance	Piceance Creek Basin	nis		Uinta	a Basin	Green River
Element	$v_{\rm ine} 1/$	Dyni2/	Donnell 3	C-a4	/2d-0	Cook 6/	Desborough et al. Z	vine1/	Easin Vine1
Potassium, % range G.M. G.D.	1.5-7.0	0.30-2.8	1	1		1	0.75-2.2	1.5-3.0	2.0-7.0
8	1.0-7.0	<1.0-17 1.2 8.02	1	!	! !	!	0.74-1.9	0.7-3.0	0.7-3.0
<b>.</b> e	.<0.030-0.2 0.15 1.66	.2 0.02-0.20 0.11 1.57	1	l I	 	0.057	0.07-0.20	0.05-0.50 0.16 1.84	0.02-0.20 0.11 1.57
barium range G.M. G.D.	30-5,000	100-1,000 300 1.60		1	ł	32	200-1,200 345	200-700 340 1.49	300-2,000 620 2.00
	<7.0-30 9.2 1.50	<3.0-20 8.3 1.67	!	!	[ 	39	5.0-20	5.0-300	<3.0-15 4.9 1.89
Chromium range G.M. G.D.	2.0-35 24 1.67	7.0-70 34 1.61	1	!	! !	64	20-70	20-70 53 1.46	15-50 33 1.56
	.<15-100 50 1.68	7.0-100 33 1.89	1	!	<b>;</b>	15	42-110 55	10-70 34 1.61	15-100 30 1.89
dailtum range G.M. G.D.	.<7.0-30 13 1.51		1	1	 	2.2	<5.0-10	10-30 18 1.39	<5.0-30 14 1.97
range G.M. G.M.	<7.0-100 12 3.57	<10-70 18 1.83	1	!	1	10	19–52 32	15-30 21 1.29	<10-30 13 1.62
range G.M.		!	1		1	850	35-208		;

Table 8.--Ranges, geometric means (GM) and geometric deviations (GD) of concentrations of selected elements in Green River oil shale from the Piceance Creck (Colorado), Uinta (Utah), and Green River (Wyoming) Basins -- Continued.

								<b></b>		-
			Piceance	e Creek Ba	sin			u	Jinta Basin	Green River
Element	Vine1/	Dyni2/	Donnell3/	C-a4/	C-b <sup>5</sup> /	Cook6/	Desbo et	rough al.2/		Basin Vine1/
Manganese range G.M. G.D. Molybdenum	<30-700 257 2.26	20-300 174 1.63		<b></b>		34	180-3 230	00	150-1,500 320 1.84	70-1,000 280 1.79
range G.M. G.D. Nickel	<5.0-3.0 11 2.11	<5.0-50 16 1.82		<b></b> i		4.9	<b>7.0-4</b>	0	<b>&lt;3.0-20</b> 5.2 2.03	<5.0
range G.M. G.D. Scandium	20- <i>6</i> 0 39 1.23	<5.0-200 18 1.66		<del>-</del> -		11	20-40 28	•	<3.0-20 22 1.67	3.0-50 15 2.29
range G.M. G.D.	<5.0-15 7.5 1.31	5.0-200 8.8 2.01				2.4	<5.0-	10	<b></b> .	
Strontium range G.M. G.D. Vanadium	10-2,000 870 2.79	20-720 300 1.51		; 		69	49-69 560	0	150-1,000 380 1.92	100-1,000 560 2.41
range G.M. G.D. Zinc	<15-200 125 1.34	20-200 109 1.53		<u></u>		29	130	00	20-100 61 1.70	20-150 62 1.74
range G.M. Zirconium						13	49-11	0		
range G.M. G.D.	<10-200 38 1.80					9.3	20-70 49		10-150 53 2.29	20-200 77 2.23

<sup>1/</sup> From unpublished data of James D. Vine (U.S. Geological Survey). Includes 36 samples of core material in the Piceance Creek Basin (sample numbers D114433-D114438; D118018-D118046), 14 samples of core material in the Uinta Basin (sample numbers D142083-D142085; D142088-D142096; D143400-D143401), and nine samples of outcrop and roadcut material in the Green River Basin (sample numbers D129429-D129430; D129454-D129459; D129665).

<sup>2/</sup> From unpublished data of John R. Dyni (U.S. Geological Survey). Includes 371 samples of core material (sample numbers D122302-D122399; D129483-D129495; D130466-D130681). Data for potassium, strontium, and sodium are based on 371 analyses; all other summaries are based on 89 analyses.

<sup>3/</sup> From unpublished data of John R. Donnell (U.S. Geological Survey). Includes 183 samples of core material (sample numbers D158971-D159153).

<sup>4/</sup> Rio Blanco Oil Shale Project (1975). Two hundred and thirty samples of fresh shale from the C-a lease tract.

<sup>5/</sup> C-b Shale Oil Project (1975). One hundred and forty samples of fresh shale from the C-b lease tract.

<sup>6/</sup> Cook (1973). One composited, pyrolized (at 500°C) sample of the Mahogany Bed at the Colony Mine.

<sup>7/</sup> Desborough and others (1976). Ten samples of oil shale from the Piceance Creek and Uinta Basins.

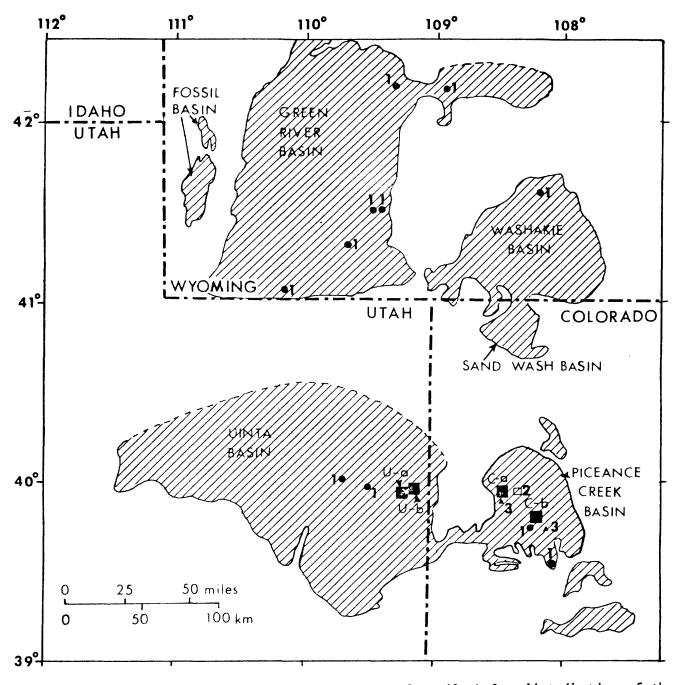


Figure 11.--Location of selected sample sites for oil shale, distribution of the Green River Formation, and lease tracts C-a, C-b, U-a, and U-b. Unpublished data of James D. Vine (1), John R. Dyni (2), and John R. Donnell (3), all of the U.S. Geological Survey, shown by symbols.

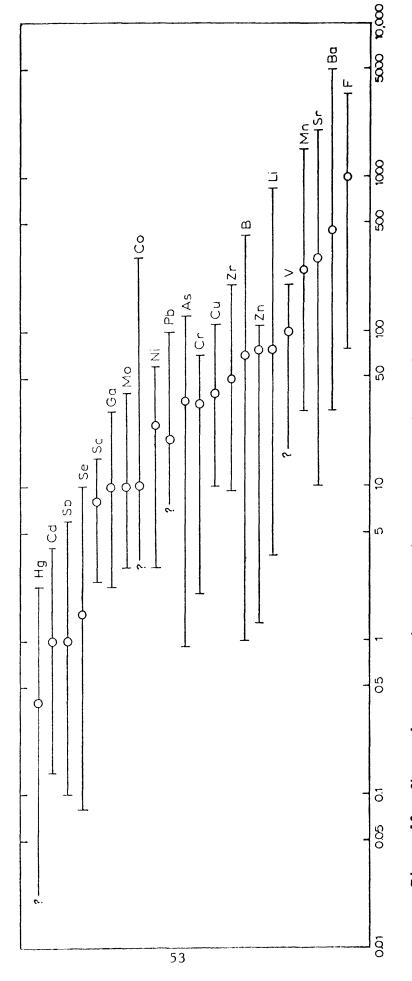


Figure 12. --Observed concentration ranges in parts per million and probable average values (open circles) for minor elements in oil shale.

#### Trace elements

The summaries in table 8 and the extant literature suggest the following notes.

<u>Cadmium</u>.--A concentration around 1 ppm would seem to be a reasonable average for Green River oil shale. The mean concentration for raw shale reported by the C-b Shale Oil Project (1975), is less than half of a part per million whereas the mean reported from the C-a tract (table 8) is over 2 ppm. Cadmium probably occurs as a substitute for zinc in minor sulfide minerals.

Antimony.--The values for antimony given in table 8 exhibit a range of <1-6 ppm. The values from the C-a tract and from Cook (1973) may be low, and Desborough and others (1976) suggest that some Sb may be volatilized during pyrolysis. An expected concentration on the order of 1 ppm antimony might be a reasonable average for raw oil shale.

Arsenic.--The C-a tract values and the single Cook value are low compared to the data of Desborough and others (1976) and the C-b tract. The low concentration (7.2 ppm) reported by Cook (1973) in pyrolized oil shale led Desborough and others (1976) to suspect that perhaps As, like Sb, may be volatilized on pyrolysis, but they could not confirm this. An expected value for arsenic on the order of 35 ppm seems reasonable. Microprobe studies by Desborough and others (1976) indicated that most of the As was present as a substitute for S in pyrite.

Mercury.--The average concentrations for mercury in table 8 all fall within a fairly narrow range, and a value of 0.4 ppm probably represents a reasonable average for oil shale. Cadigan (1970) reported a median concentration of 0.1 ppm Hg in 260 samples from the Uinta and Green River Formations of the northern Colorado Plateau. Donnell's samples included ten each of raw and pyrolized oil shale from the same core intervals. The geometric mean concentrations of Hg in the fresh and spent shale were 3.7 and 3.1 ppm respectively indicating that little Hg is lost on pyrolysis.

Selenium. -- The means for selenium in oil shale from the C-b tract and from Desborough and others, suggest an average concentration on the order of about 1.5 ppm. Selenium may substitute for sulfur in sulfide minerals, but may also occur as elemental selenium in a number of organic compounds.

<u>Fluorine</u>.--Mean concentrations of fluorine in oil shale listed in table 8 range from 550-1,300 ppm; a value of about 1,000 ppm would appear to be a reasonable concentration for fluorine in an average oil shale sample. Microprobe studies by Desborough and others (1976) show that F occurs as 5- to  $10\text{-}\mu\text{m}$  grains of fluorite and cryolite disseminated within the shale.

Boron.--Mean values for boron listed in table 8 range from 22 to over 100 ppm, and average about 70 ppm. Desborough and others (1976) concluded that boron resides in K-feldspar disseminated throughout the Green River Formation.

<u>Barium</u>.--Table 8 suggests that a concentration on the order of 450 ppm barium is a reasonable average for typical Green River oil shale, although values of several thousand ppm (that is, several tenths of a percent) should not be surprising. The most probable mineral residence of Ba is in barite. Barite is a common diagenetic mineral in marine sediments, especially in organic-rich sediments (Church and Wolgemuth, 1972; Cronan, 1974; Dean and Schreiber, 1976).

Cobalt, Chromium, and Copper.--Suggested concentrations of these three elements in the average Green River oil shale are on the order of 10 ppm for cobalt, 35 ppm for chromium, and 40 ppm for copper. Cook's value of 39 ppm cobalt appears to be too high while his value of 15 ppm for copper appears to be too low. All three of these elements are probably present as substitutes for iron in pyrite (Desborough and others, 1976).

<u>Gallium</u>.--The data in table 8 suggest typical concentration on the order of 10 ppm gallium.

<u>Lead</u>.--Most of the data for lead falls within a fairly narrow range and suggests an average concentration in oil shale of about 20 ppm. Lead probably resides in a sulfide phase, either as a separate trace sulfide or substituting for iron in pyrite.

Lithium and zinc.--The only values for lithium and zinc listed in table 8 are those by Desborough and others (1976) and Cook (1973) who give markedly contrasting figures. Desborough's data suggest that average oil shale probably contains less than 100 ppm each, perhaps 75 ppm. Desborough and others (1976) report correlations between lithium and fluorine, calcium, and magnesium, suggesting that lithium is associated with one or more carbonate phases.

Manganese.--Except for Cook's value of 34 ppm, the data on the manganese in oil shale suggest a typical concentration on the order of 250 ppm. According to Desborough and others (1976), the main occurrence of manganese in oil shale is substitution for iron in ferroan dolomite, siderite, and magnesiosiderite.

Molybdenum and Nickel.--Most of the values for molybdenum in oil shale lie between <5 and about 20 ppm, suggesting an average concentration of perhaps 10 ppm. Nickel concentrations tend to fall within a fairly narrow range of 15 to 40 ppm, with an average of about 25 ppm. Desborough and others (1976) report general correlations between both Mo and Ni and sulfide-S, suggesting that the dominant residences for both elements are in sulfide phases, probably substituting for iron in pyrite.

Scandium. -- The limited values for scandium suggest an average value for oil shale of about 8 ppm.

Strontium. -- The data for strontium in table 8 range from 10 to 2,000 ppm. The values of Desborough and others (1976) and Dyni were obtained by atomic absorption and probably represent more reliable results than those obtained by semiquantitative optical emission spectrometry (Vine's samples), and an average of about 300 ppm is provisionally suggested. Most of the Sr in oil shale probably occurs as a substitute for Ca in calcite and dolomite.

<u>Vanadium</u>.--Concentrations of vanadium show considerable variation, and this probably reflects variation in amount of, and concentration of vanadium in, organic material within the Green River Formation. A mean value of about 100 ppm seems reasonable. The value of 29 ppm V in Mahogany zone oil shale from the Piceance Creek Basin reported by Cook (1973) appears low, although this may reflect the fact that his sample was pyrolized prior to analysis.

Zirconium.--Most zirconium concentrations in table 8 fall between 10 and 200 ppm, and an average of about 50 ppm seems reasonable. Again, the value of 9.3 ppm reported by Cook (1973) appears a little low. Desborough and others (1976) suggested that most of the Zr in the Green River Formation probably occurs as zircon.

# CHEMISTRY OF NORTHERN GREAT PLAINS SOILS by Ronald R. Tidball and Ronald C. Severson

The sample design employed and some preliminary data from a reconnaissance study of total chemical composition of soils in the Northern Great Plains Coal Province were described in U.S. Geological Survey (1975, p. 36-49). Additional analytical results are given here. We are repeating the data summaries presented in the 1975 report in order to reflect an alternate interpretation of the analytical error variance. In brief, we have estimated the analytical-error variance component separately for both the A-horizon and the C-horizon, by including the duplicate analyses as an incomplete 6th level in the nested analysis of variance (ANOV) design of the entire data set, as follows:

Number	ΟÍ	units	at	each	level

					Analyt	ical
Terrain	100km	50km	10km	1km	A-horizon	C-horizon
Glaciated Unglaciated	12 22	24 44	36 66	48] 88]	12	16
Total	34	68	102	136	148	152

Analysis of variance

		Degrees of freedom			
Leve1	Source of variation	A-horizon	C-horizon		
1	Between terrains	2-1=1	2-1=1		
2	Between 100-km cells	34-2=32	34-2=32		
3	Between 50-km cells	68-34=34	68-34=34		
4	Between 10-km cells	102-68=34	102-68=34		
5	Between 1-km cells (samples)	136-102=34	136-102=34		
6	Between analyses	148-136=12	152-136=16		
	Total	148-1=147	152-1=151		

The degrees of freedom are computed according to Anderson and Bancroft (1952, p. 328). Variance components for all elements reported to date are given in table 9.

The distribution of the components indicates that for most elements the greatest percentage of variance occurs at the local level within areas with dimensions up to 10 km on a side. The analytical error for several elements exceeded 50 percent of the total variance and was, therefore, judged to be excessive. No interpretation is given for such elements. Of the remaining 54 entries, 28 exhibit significant (at 0.05 probability level) differences between glaciated and unglaciated terrain. Several elements are also significantly different between areas that are 50 or 100-km on a side. The variance components are used to compute the variance mean ratio.

Table 9.--Variance components expressed as percentage of total variance in samples of two horizons of soils from the Northern Great Plains, and variance mean ratio,  $v_{m^{\pm}}$  for 100-km cells

[\*, significant at 0.05 level]

Element	Soil horizon	Total log10 variance	Between terrains	Between 100-km cells	Between 50-km cells	Between 10-km cells	Between 1-km cells	Analytical error	v <sub>ax</sub>
A1	A	0.0069	11.7*	0	32.3*	3.3	31.7*	21.0	0.34
	С	.0106	11.0*	0	16.2	0	66.9*	5.9	.39
В	A	.0446	0	8.8	0	48.9*	18,4	23.9	.30
	С	.0466	0.7	10.2	0	12.1	69.7*	7.3	.46
Ва	A	.0175	0	6.3	0	3.1	3.2	87.5	.26
	С	.0629	0	9.0*	0	21.9*	0	69.1	.35
Be	A	.0340	6.4*	0.03	6.4	0	55.7*	31.4	.25
	С	.0477	1.3	0	52.1*	0	28.9*	17.6	.03
C	A	.0444	25.6*	20.7*	0	4.7	48.5*	•5	3.3
	С	.1293	21.2*	12.5*	0	13.6	52.1*	.6	1.8
Ca	A	.1586	0	18.8*	0	21.3	59.5*	.4	.82
	С	.1166	26.4*	4.0	4.6	7.2	57.4*	.4	1.5
Co	A	.0400	0	0	49.0*	. 3.5	25.0	22.5	0
	С	.0411	.6	0	24.9	0	58.5*	16.0	.02
Cr	A	.0434	0	17.2*	0	0	15.3	67.5	.83
	С	.0679	.7	0	32.2*	0	42.0*	25.1	.02
Cu	A	.0470	•7	0	22.7	2.8	44.5*	29.4	.02
	С	.0877	0	0	17.8	0	48.2*	34.0	0
F	A	.0827	2.4*	11.8*	5,4	0.	0	80.4	.60
	С	.0693	.1	0	0	26.2*	0	73.7	<.01
Fe	A	.0329	0	18.1*	0	62.9*	18.6*	.4	.64
	С	.0291	0	0	20.2*	0	79.5*	•3	0
Ga	A	.0287	3.0	0	10.4	0	42,5	44.0	.11
	С	.0565	2.0*	0	29.2*	0	41.3*	27.6	.06
не	A	.0672	6.4*	4.8	0	55.0*	2.9	30.9	.39
	С	.0736	3.8	3.7	6.3	0	82.9	3.3	.29
K	A	.0038	43.7*	0	13.3	4.4	36.6*	2.0	2.2
	С	.0033	39.6*	0	21.6*	2.4	35.9*	.5	1.7
La	A	.0353	2.7	0	0	9.4	30.3	57.5	.11
	С	.0558	.4	0	15.9	0	45.3*	38.4	.01
Li	A	•0209	3.0	4.1	11.1	.1	79.1*	2.6	.26
	С	.0440	0	0	25.4	0	68.2*	6.4	0
Mk	A	.0477	0	5.2	40.3	18.8	35.5*	.2	.13
	С	.0620	10.7*	17.2*	0	27.6*	44.4*	.1	1.3
Min	A	.1851	22.6*	0	0	33.0*	8.2	36.2	.96
	С	.2361	10.6*	3	34.1*	4.2	24.3	26.8	.30

Table 9.--Variance components expressed no percentage of total variance in samples of two horizons of soils from the Northern Great Plains, and variance mean ratio, v<sub>m</sub>, for 100-km cells -- Continued

Element	Soil horizon	Total log	Between terrains	Botween 100-ium cells	Between 50-km cells	Between 10-km cells	Between 1-km cells	Analytical error	V <sub>B</sub>
Но	A	0.1068	0.5	7.8*	11.1	0	44.4	36,2	.31
	с	.1860	0	0	32.5*	0	25.7	41.8	0
Na1/	٨	. 0774	7.7	19.5*	10.1	0	62.2 *	.5	1.2
	C	.1249	1.6	7.2	0	29.2	61.1*	.9	.33
Nb	A	.0510	.7	0	19.1*	0	24.5	55.7	.02
	C	•0600	0	0	21.3	18.8	0	59.9	0
Ni	A	•0275	0	11.0*	0	12.3	40.6	36.0	.46
	C	.0519	3.8*	0	20.8	0	58.2*	17.2	.12
P	A	.0319	0	1.1	5.7	0	0	93.2	.04
	c	.0281	0	0	17.9	0	4.9	77.2	0
Pb	A	.0396	1.9	0	9.9	0	26.6	61.6	.07
	c	.0826	.1	0	39.6*	0	35.4*	24.9	<.01
Rb	A	.0093	25.0*	11.1*	0	29,2*	24.8*	9.9	1.8
	C	.0186	31.2*	0	3,3	9,4	49.3*	6.8	1.6
Sc	A	.0622	0	9.1	0	6.9	21.3	62.2	.39
	С	.0772	2.2	0	22.9	0	5.8	69.1	.07
s <u>i</u> l/	٨	9,531	0	27.0*	0	7.6	52,0*	13.4	1.4
	C.	12.61	6.9*	9.3	0	7.3	64.7*	11.8	•74
Sr	A	.0295	8.8*	2.1	. 0	37.5*	33.4*	18.3	.40
	c	.0372	9.3*	6.1	0	0	75 <sub>4</sub> 8*	8.8	.73
Th	Å	.0094	17.7*	5.5	0	29.2*	23.5	24.1	1,0
	c1/	.0208	13.3*	0	2.2	16.5	17.1	50.9	.54
T11/	A	.0023	0	11.2	0	39.9*	32.2*	16.7	.41
•	С	.0041	1.3	0	6.4	0	87.4*	4.9	.05
U	A	.0131	31.7*	10.2*	0	18.0	37.6*	2.5	2,5
	С	.0288	17.7*	0	10.6	11.5	57.9*	2.3	.68
٧	A	.0171	7.3*	0	3.1	12.6	22.1	54.9	.28
	С	.0449	10.7*	0	17.5*	0	60.6*	11,2	.37
Υ	A	.0369	2.2	7.1	0	0	47.2	43.5	.41
	С	.0361	o	0	0	30.9*	29.1	40,1	0
Yb	٨	.0296	6.4*	0	9.0	0	3.3	81.3	.24
	С	.0347	1.2	0	0	26.7*	24.5	47.6	.04
z <u>n1</u> /	A	540.2	3.3	19.0*	0	13.4	62.4*	1.9	1.1
	c	413.5	0	0	10.7	0	74.9*	14.4	0
Zr	٨	.0594	4.6*	8.5	0	10.0	0	76.6	.59
	С	.0405	o	5.0	4.2	0	22.9	67.9	2.0

<sup>1/</sup> Variance computed on arithmetic basis.

#### Variance mean ratio

The variance mean ratio,  $v_m$ , of Miesch (1976) provides an index of the relative stability of the estimate of the mean of any given cell size based on the data already collected. In particular we use  $v_m$  to evaluate the feasibility of mapping the regional distribution of elements using means computed for 100-km cells. We require that  $v_m$  equal or exceed a value of 1.0 for such maps. The equation for  $v_m$  has been modified from that of Miesch to account for the staggered, nested design (U.S. Geological Survey, 1975, p. 39), as follows:

$$v_{\rm m} = \frac{P_{\rm T} + P_{100}}{a_{50}P_{50} + a_{10}P_{10} + a_{1}(P_{1} + P_{e})}$$

where the subscripted P's are the percentages of total variation in table 1 corresponding to terrains, 100-km cells, 50-km cells, 10-km cells, 1-km cells (samples), and analytical error, respectively. The denominator is the variance of the mean of 100-km cells. The coefficients,  $a_i$ , which represent the average numbers of samples in each level of the design, are developed from the general expression of Leone and others (1968), p. 725),

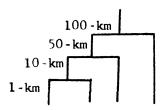
$$a_i = \frac{n_1^2 + n_2^2 + \cdots n_x^2}{N^2}$$

where  $n_1$ ,  $n_2$ , and so forth are the numbers of samples within each unit of a level, and N is the total number of samples within the level.

The computations are illustrated in figure 13 for each coefficient in the equation for v (above). The necessity to sum the two lowest variance components ( $P_1+P_e$ ) stems from the irregular distribution of the analytical duplicates through the staggered sample design. The inability to treat  $P_e$  as a separate term here results in a slight artificial inflation of the value for  $v_m$ .

## 100-km cell without analytical

## duplicates, staggered design



Analytical error variance,  $P_e$ , is estimated from duplicates, as follows:

A-horizon, 12 duplicate pairs

C-horizon, 16 duplicate pairs

### Coefficients:

$$a_{50} = \frac{\Sigma \text{ (no. in 50-km cell)}^2}{\text{ (no. in 100-km cell)}^2}$$
$$= \frac{3^2 + 1^2}{4^2} = .63$$

$$a_{10} = \frac{2^2 + 1^2 + 1^2}{4^2} = .375$$

$$a_1 = \frac{4(1^2)}{4^2} = 25$$

Figure 13.--Computation of coefficients,  $a_i$ , for the variance mean ratio,  $v_m$ .

#### Element distributions

The elements shown in table 9 have been placed into one of five groups on the basis of significant variance components and the value of  $v_m$ . The groups are, as follows:

- (A) Elements with  $v_{\rm m}$  less than one:
  - (a) Without significant variance at the terrain level;
    - (1) Without significant variance at the 100-km level--

elements included are boron, cobalt, copper, gallium, lithium, magnesium, titanium, and yttrium in A-horizon, and boron, beryllium, cobalt, chromium, copper, iron, lanthanum, lead, lithium, mercury, molybdenum, sodium, titanium, yttrium, ytterbium, and zinc in C-horizon.

- (2) With significant variance at the 100-km level-elements included are calcium, iron, molybdenum, and nickel in A-horizon.
- (b) With significant variance at the terrain level; elements included are aluminum, beryllium, manganese, mercury, and strontium in A-horizon, and aluminum, gallium, manganese, nickel, silicon, strontium, uranium, and vanadium in Chorizon.
- (B) Elements with  $v_m$  equal to or greater than one:

elements included are carbon, potassium, rubidium, sodium, silicon, thorium, uranium, and zinc in A-horizon, and carbon, calcium, potassium, magnesium, and rubidium in C-horizon.

(C) Elements with excessive analytical error:

elements included are barium, chromium, fluorine, lanthanum, lead, niobium, phosphorus, scandium, vanadium, ytterbium, and zirconium in A-horizon, and barium, fluorine, niobium, phosphorus, scandium, thorium, and zirconium in C-horizon.

The elements of group A(a)1 exhibit no significant differences between either terrains or 100-km cells. A single grand mean and deviation based on all observations is, therefore, the best regional estimate of central tendency for those elements. The means, deviations, analytical errors, and 95-percent expected ranges for this group are given in table 10. The expected range is computed following adjustment of the gross geometric deviation (GD) for the analytical error (GE) as described on the inside cover of this report. For data that were not logarithmically

Table 10.--Geochemical summaries for elements of group (A) in soils of the Northern Great Plains

[G, glaciated terrain; U, unglaciated terrain; elements of group A(a) which do not differ between terrains are given only one value under Mean, Deviation, and Baseline; elements of group A(b) which exhibit significant differences between terrains have a value under G and U, respectively; n<sub>r</sub>, minimum number of random samples per 100-km cell needed to map regional variation; n.d., not determined, n<sub>r</sub> is indefinitely large]

Element	Soil Horizon	Geometr mear G	1	Geome devia		Geometric error	Expected (base)		nr
Al	A	5.3	8.5	1.17	1.18	1.09	4.1-6.9	4.4-7.7	7
	С	5.3	5.9	1.22	1.22	1.06	3.6-7.8	4.0-8.6	7
B, ppm	A	41		1.	<b>5</b> 9	1.27	18-9	96	9
	С	43		1.	61	1.14	16-	115	7
Be, ppm	A	1.45	1.71	1.46	1.38	1.27	0.81-2.6	1.1-2.6	11
	С	1.6		1.	44	1.23	•64-	4.0	n.d.
Ca	A	1.0		2.	14	1.06	.22-	4.6	5
Co, ppm	A	6.4		1.	48	1.24	2.8-	14.3	n.d
	С	6.6		1.	49	1.21	2.8-	15.5	n.d
Cr, ppm	C	42			66	1.35	15-		n.d
•	A	19			64	1.31	8.0-		n.d
Cu, ppm						•			
	С	17			82	1.49	5.7-		n.d
Fe	Α	2.1		1.	41	1.02	1.1-	4.2	5
	C	2.2		1,	40	1.02	1.1-	1.43	n.d
Ga, ppm	A	11		1.	44	1.30	6.0-	19	28
	С	10 1	1	1.58	1.51	1.33	5.0-21	6.2-21	34
Hg, ppb	A	26 23	1.	1.40	1.79	1.39	22-30	8-55	7
	С	27		1.	74	1.12	10-	80	10
La, ppm	С	23		1.	55	1.38	10-	51	n.d
Li, ppm	A	19		1.	40	1.06	9.8-	37	11
	С	21		1.	48	1.13	10-	46	n.d

Table 10.--Geochemical summaries for elements of group (A) in soils of the Northern Great Plains -- Continued.

Element	Soil horizon	Geometric mean G U	Geometric deviation G U	Geometric error	Expected 95% range (baseline)	n <sub>r</sub>
Mg	A	0.66	1.67	1.02	.23-1.8	14
Mn, ppm1/	A	720 330	1.83 2.76	1.81	570-910 60-1,700	5
	С	440 180	2.37 4.20	1.79	120-1,600 10-2,500	8
Mo, ppm	A	3.8	1.68	1.57	1.1-12.6	9
	c	4.0	1.72	1.90	.87-18.0	n.d.
Na_2/	c	.85	0.33	0.034	.19-1.5	9
Ni, ppm	A	18	1.46	1.26	10-32	7
	C	22 18	1.44 1.67	1.24	12-40 7-46	16
Pb, ppm	С	15	1.71	1.39	4.7-47	n.d.
si <sup>2</sup> /	C	27 29	2.74 3.59	1.22	22-32 22-36	5
Sr, ppm	A	185 152	1.24 1.54	1.18	140-244 68-337	7
	С	236 192	1.24 1.56	1.14	168-381 82-449	6
Ti <sup>2</sup> /	A	.25	.023	.019	.22-0.28	7
	С	.25	.058	.014	.1436	32
U, ppm	C	2.2 2.	8 1.42 1.41	1.06	1.1-1.4 1.4-5.5	5
V, ppm	C	64 50	1.45 1.43	1.18	33-124 26-99	7
Y, ppm	A	18	1.46	1-34	9.5-36	8
	C	17	1.47	1.32	8.5-33	n.d.
Yb, ppm	C	2.1	1.49	1.34	1.1-3.9	n.d.
Zn, ppm <sup>2</sup> /	C	<b>5</b> 9	19	7.7	23-94	n.d.

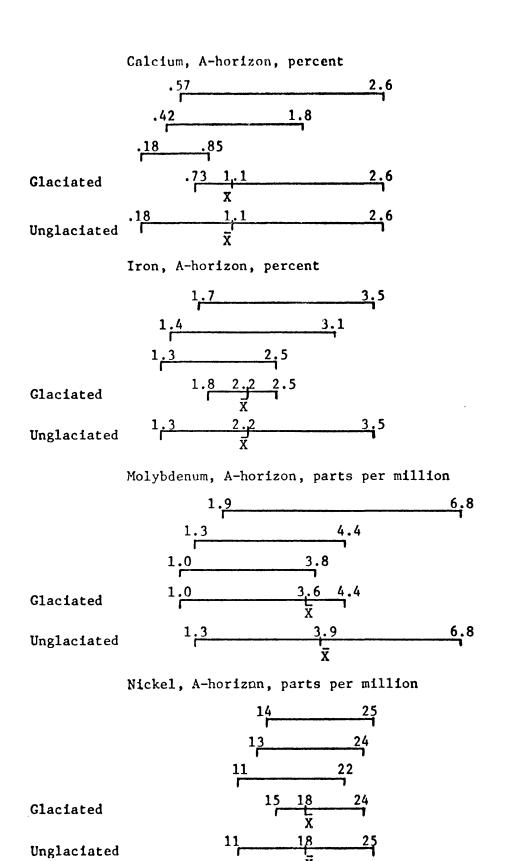


Figure 14.--Duncan's classes for elements of group A(a)2 and observed ranges of 100-km cell means for each terrain.

[X, terrain mean.

transformed (where SD is standard deviation and SE is standard error of analysis), the expected 95-percent range is computed as,

AM - 
$$2(SD_n)$$
 to AM +  $2(SD_n)$ 

Here, AM is the arithmetic mean and  ${\rm SD}_{\rm n}$  is computed from the standard deviation (SD) and the standard error (SE) as follows:

$$SD_n = [(SD)^2 - (SE)^2]^{\frac{1}{2}}$$

The elements of group A(a)2 are shown in figure 14 as the shortest significant ranges (classes) for distinguishing among cell means according to Duncan's multiple range test (Duncan, 1955). The array of cell means for a given element has been grouped into classes, each with the shortest significant range. That is, each class contains means that are not significantly different from each other. In essence, the largest value of the class does not differ from the smallest value. For example, the mean for calcium in the glaciated terrain does not differ from that of unglaciated terrain, but ANOV indicates that the means of 100-km cells within each terrain are significantly different from each other. This suggests that the measure of central tendency is best estimated by the local cell mean. It can be seen in figure 14, however, that significant differences between 100-km cell means do exist in unglaciated terrain for calcium. Therefore, the terrain mean of 1.1 percent is the best estimate for calcium in A-horizon soil in glaciated terrain, and local cell means are better estimates within the unglaciated terrain, but with the constraint that these cell means require additional sampling before they can be viewed as "stable" (because  $v_m$  is less than one). Because maps of these elements would be unstable, the only useful summary based on the data at hand is that for the entire area. Consequently, these elements are summarized in table 10 along with the A(a)1 elements.

The elements of group A(b) exhibit a significant difference between terrains but no significant difference between 100-km cells within the terrains. The best estimate of central tendency for these elements is given by separate means, one for glaciated and one for nonglaciated terrain. These means, deviations, analytical errors, and 95-percent expected ranges are also given in table 10.

Elements in group (B) all have  $v_m$  greater than one, which indicates that the means of 100-km cells are minimally stable estimates. The geographic distribution of these cell means is presented in the form of maps in figures 15 to 27.

We have ventured to draw contours on the cell means merely as an aid to quickly visualizing the distributions. We do so with the know-ledge of at least two deficiencies--first, the contours are very subjective and represent only one of several possible patterns; and second, a known gradient is implied for all possible points between adjacent

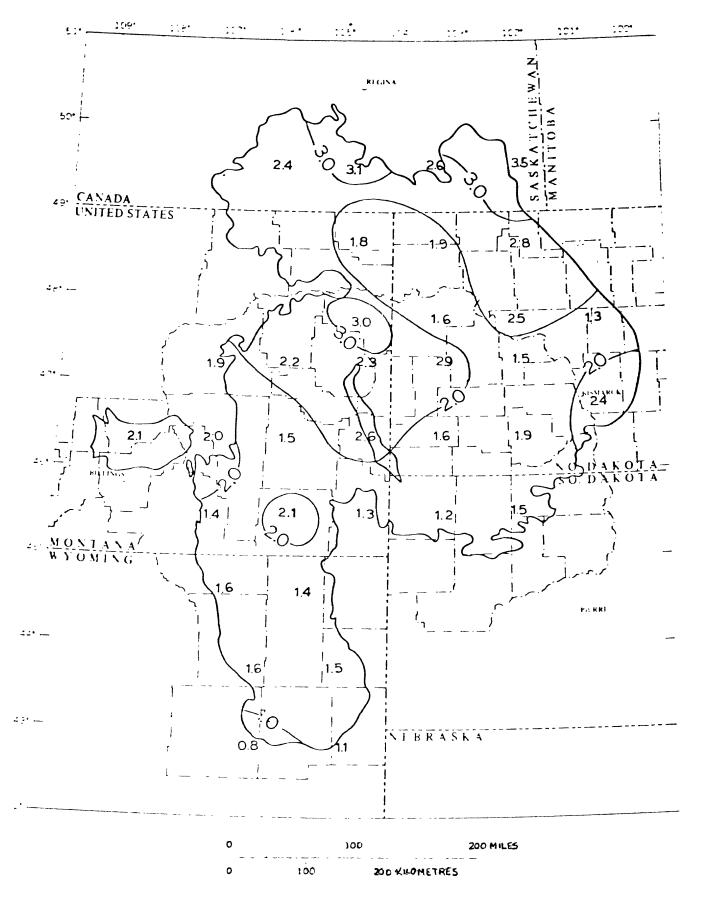


Figure 15.--Regional distribution of carbon (total) in A-horizon soils of the Northern Great Plains. Values (percent) are means of 100-km cells. Stability index  $(V_m)$  is 3.3.

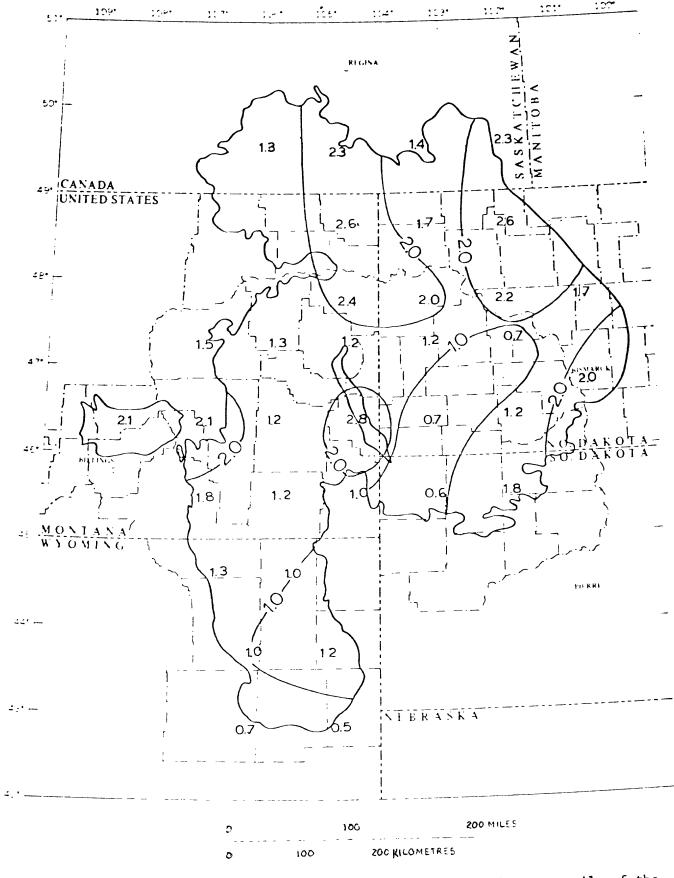


Figure 16.--Regional distribution of carbon (total) in C-horizon soils of the Northern Great Plains. Values (percent) are means of 100-km cells. Stability index ( $V_{\rm m}$ ) is 1.8.

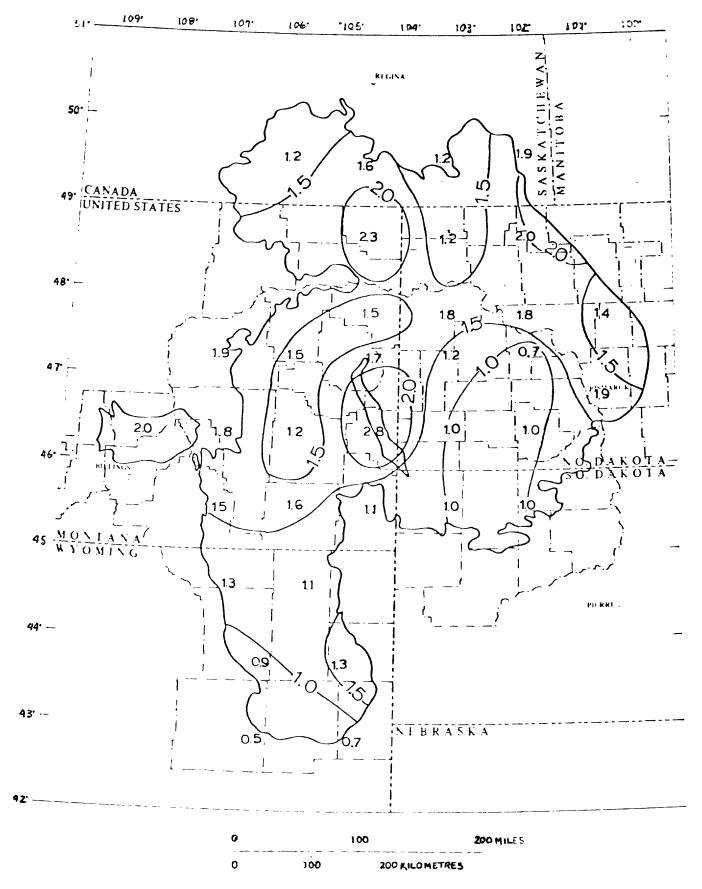


Figure 17.--Regional distribution of magnesium in C-horizon soils of the Northern Great Plains. Values (percent) are means of 100-km cells. Stability index ( $V_m$ ) is 1.3.

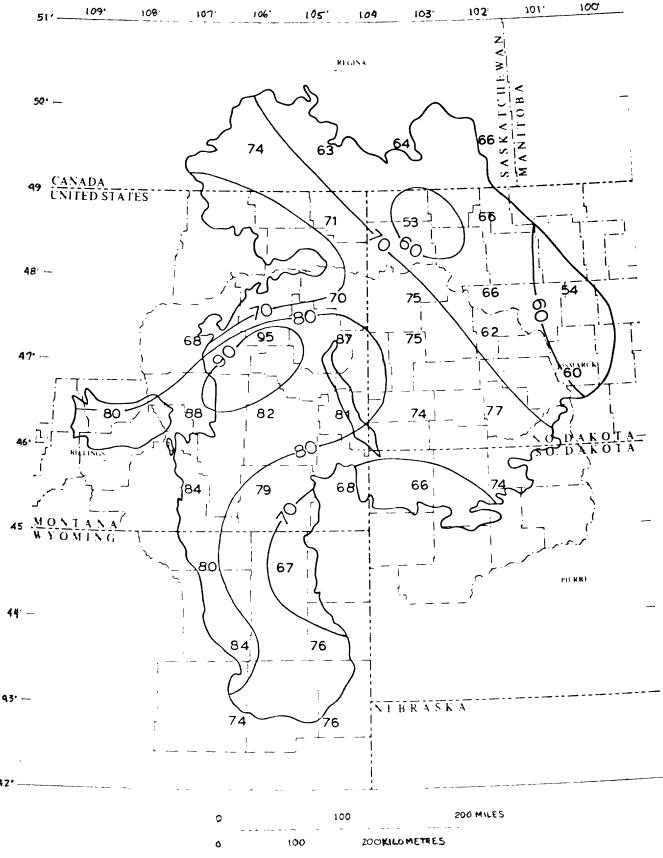


Figure 18.--Regional distribution of rubidium in A-horizon soils of the Northern Great Plains. Values (ppm) are means of 100-km cells. Stability index is 1.8.

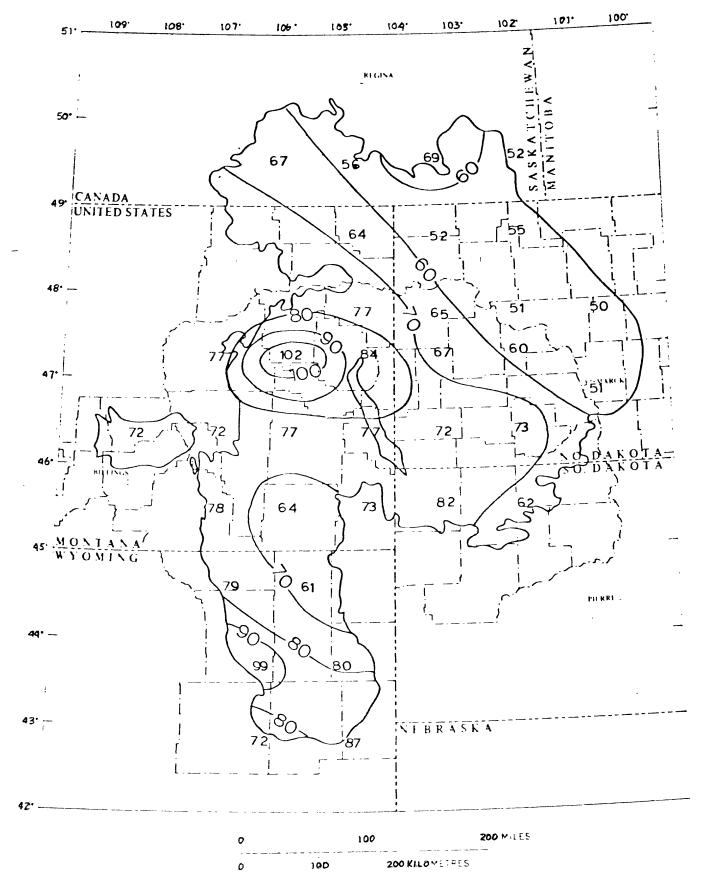


Figure 19.--Regional distribution of rubidium in C-horizon soils of the Northern Great Plains. Values (ppm) are means of 100-km cells. Stability index  $(V_m)$  is 1.6.

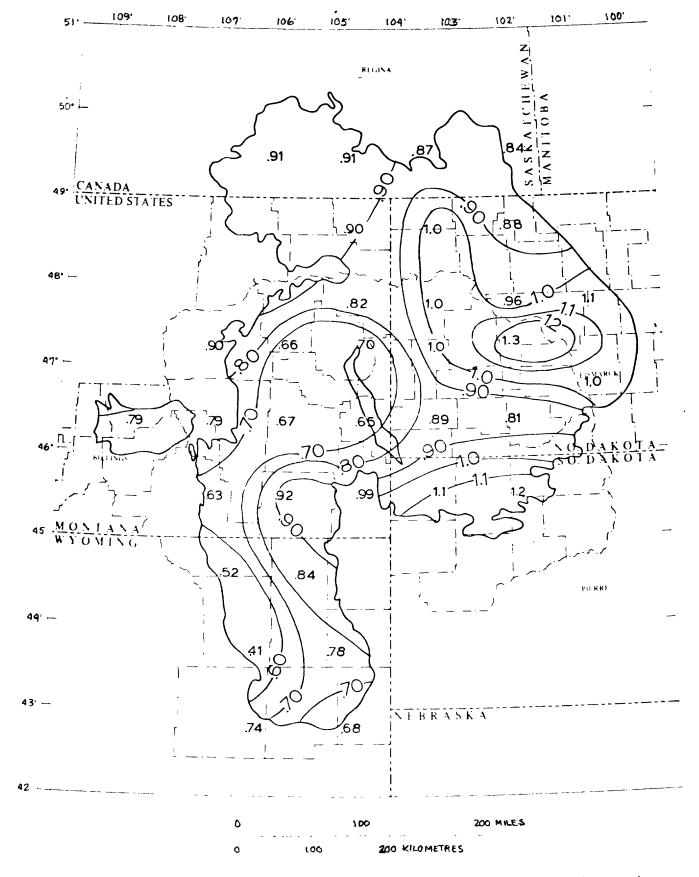


Figure 20.--Regional distribution of sodium in A-horizon soils of the Northern Great Plains. Values (percent) are means of 100-km cells. Stability index ( $V_m$ ) is 1.2.

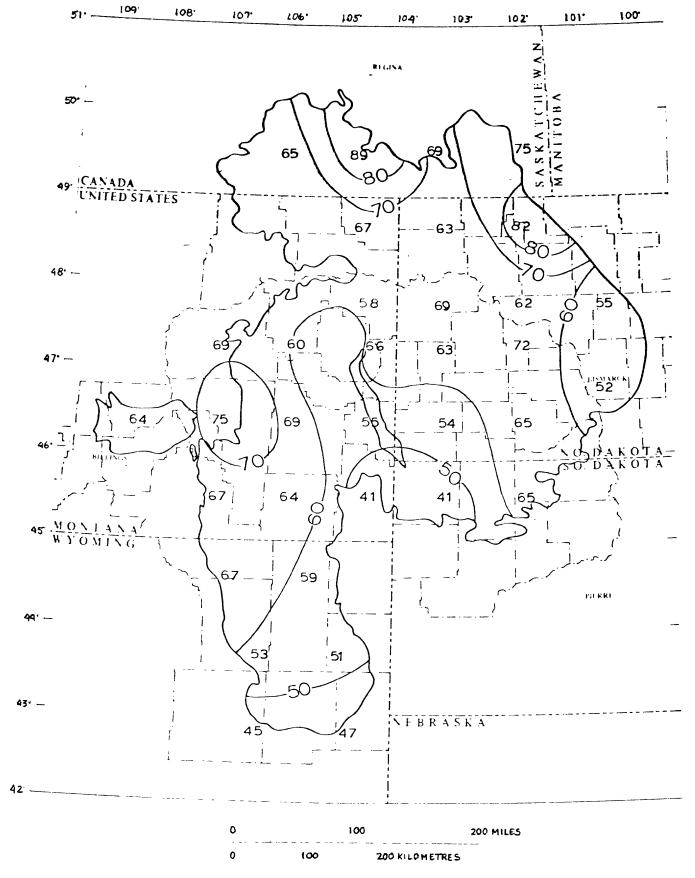


Figure 21.--Regional distribution of zinc in A-horizon soils of the Northern Great Plains. Values (ppm) are means of 100-km cells. Stability index is 1.1.

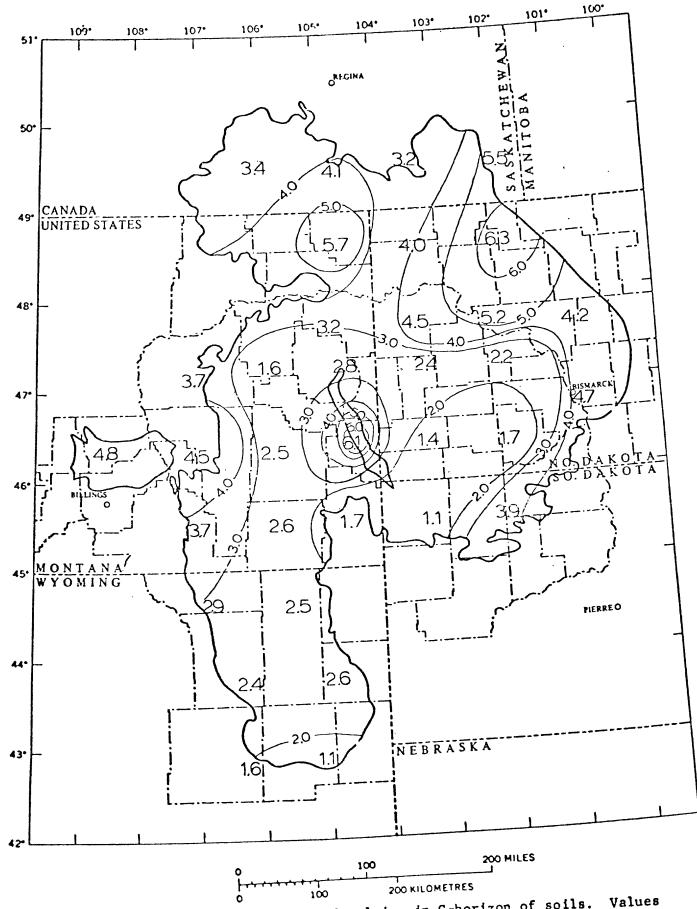


Figure 22. Regional distribution of calcium in C-horizon of soils. Values (percent) are means of 100-km cells. Stability index  $(V_m)$  is 1.5.

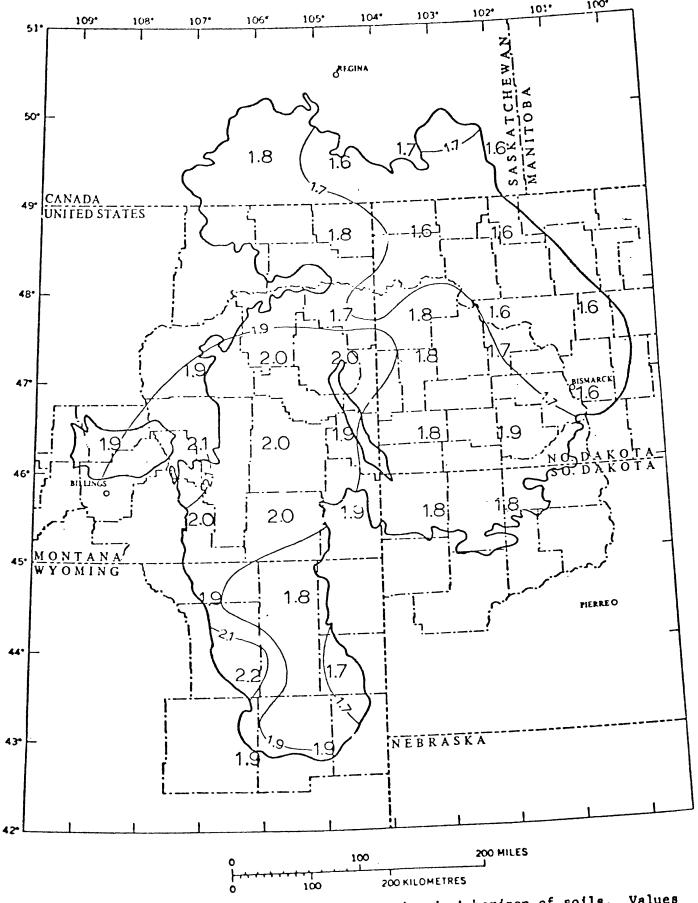


Figure 23. Regional distribution of potassium in A-horizon of soils. Values (percent) are means of 100-km cells. Stability index  $(V_m)$  is 2.2.

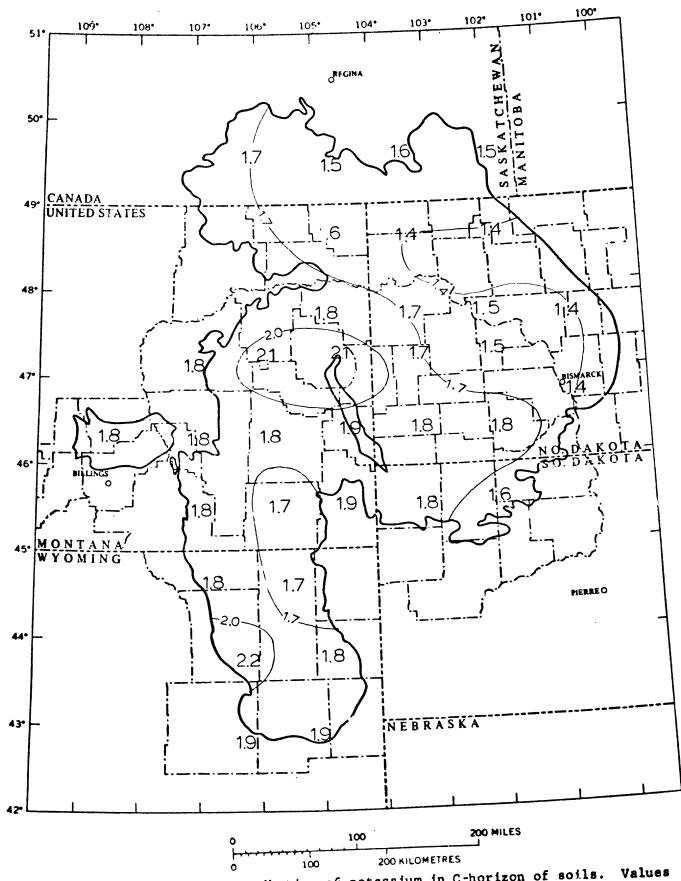


Figure 24. Regional distribution of potassium in C-horizon of soils. Values (percent) are means of 100-km cells. Stability index  $(V_m)$  is 1.9.

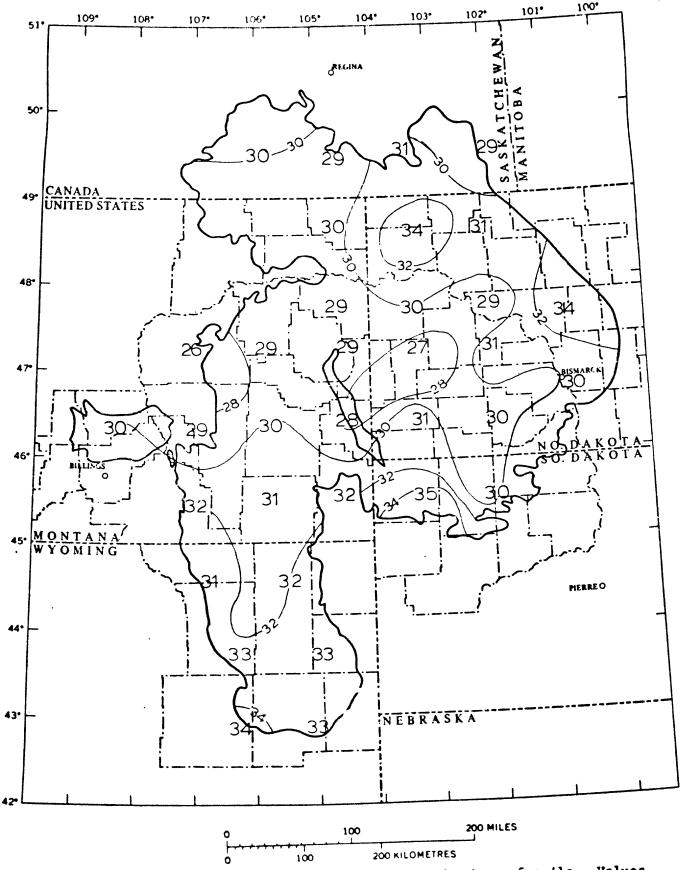


Figure 25. Regional distribution of silicon in A-horizon of soils. Values (percent) are means of 100-km cells. Stability index  $(V_m)$  is 1.5.

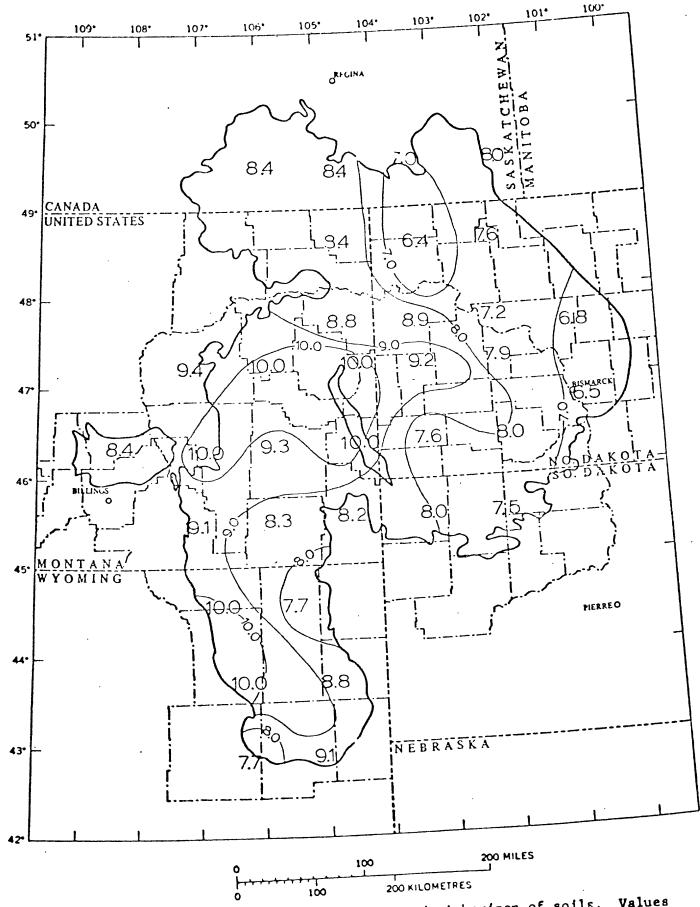


Figure 26. Regional distribution of thorium in A-horizon of soils. Values (ppm) are means of  $100-\mathrm{km}$  cells. Stability index ( $V_m$ ) is 1.0.

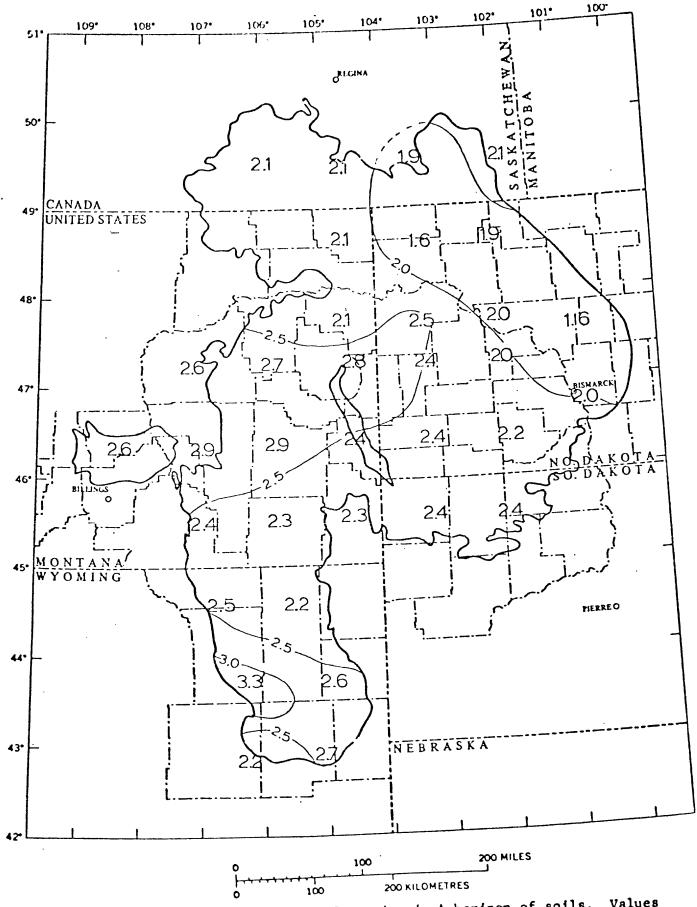


Figure 27. Regional distribution of uranium in A-horizon of soils. Values (ppm) are means of 100-km cells. Stability index ( $V_m$ ) is 2.5.

contours which is not always correct. In fact, the maps represent varying degrees of detailed information depending on the magnitude of differences between adjacent 100-km cell means.

#### Sampling requirements

Estimates of 100-km cell means based on the preliminary sampling are unstable (v is less than one) for some elements. This indicates that additional sampling is required to improve the estimates. How many samples are necessary? The required number of samples, n, is given in table 10. The value, n, is computed according to methods described by Miesch (1976) and represents the number of samples that should be randomly selected within each 100-km cell to estimate a stable mean at the 80 percent confidence level. It should be understood that n is a minimum estimate and it would be advisable to exceed that number for a margin of safety. The value, n cannot be estimated for several elements because the numerator in the ratio, v, is estimated as zero; however, n must be a large number. It may be impractical to estimate a cell mean for these elements because of the sampling and analytical cost.

#### Error variance

Because a single sample, subjected to repeated chemical analysis would not yield identical results, it is appropriate to estimate the error variance associated with sample preparation and analysis. Such error is a part of the total variation observed in the sample of a population and, in some cases, it exceeds the variation from any other source. The matrix composition of some samples may be such that interferences with the determination of some element or suite of elements result in large differences in reproducibility of a reported value. In these cases, the usual procedure is to estimate the analytical variation for each suite of samples after they have been grouped according to similar matrix compositions.

In the unbalanced, nested, analysis-of-variance design used in the study, the sixth (or lowest) level consists of samples that were analyzed in duplicate to estimate variation associated with sample preparation and analysis. This sixth level was incomplete, however, consisting of 12 surface- and 16 subsurface-soil-horizon samples, each split into two parts. Initially we assumed that variance analyses of the surface- and subsurface-horizon samples could be combined to yield one estimate of analytical variation for each element. This assumption was based on the knowledge that both the surface- and subsurface-horizon samples were composed of materials with varying matrix compositions (for example--Pleistocene sediments such as glacial till, lacustrine sediments, loess, and outwash; Tertiary sediments such as sandstone, siltstone, and alluvium). Therefore, any matrix effects that would tend to decrease the reproducibility of an analytical procedure should be common to both surface and subsurface horizons. However, the error variances in table 9

suggest that for many elements, the analytical reproducibility differs widely in the two soil horizons. In fact, the logarithmic variance estimates of analytical error for B, Ba, C, Hg, Li, Na, Th and Zn are significantly different as shown in the following table of F-ratios.

Element	F-ratio	Element	F-ratio	Element	F-ratio	Element	F-ratio
A1	2.42	Fe	1.39	Nb	1.27	Ti	2.11
В	3.12*	Ga	1.24	Ni	1.11	U	2.05
Ва	2.84*	Hg	8.60*	P	1.37	V	1.88
Ве	1.27	K	1.63	Pb	1.18	Y	1.10
С	3.36*	La	1.04	RЪ	1.38	Yb	1.46
Ca	1.55	Li	5.19*	S	2.00	Zn	5.88*
Co	1.36	Mg	2.65	Sc	1.38	Zr	1.65
Cr	1.72	Mn	1.01	Si	1.16		
Cu	2.16	Mo	2.01	Sr	1.64		
F	1.30	Na	3.30*	Th	4.64*		

The ratio is computed for each element by dividing the variance of the surface or subsurface horizon, whichever is larger, by the smaller variance. Ratios with an asterisk are significantly different from 1.0 at the 0.05 probability level. Because 29 elements do not show significant differences, it appears that some properties or factors other than matrix composition are affecting the reproducibility of the analytical determinations. If the analytical technique is at fault, then we would expect that a group of elements determined by a single technique should consistently exhibit either significant or nonsignificant variation between horizons. However, the elements that exhibit significant differences between errors in the two horizons were determined by a number of procedures (cf. U.S. Geological Survey, 1975, fig. 2).

As a general recommendation, the investigator should be aware of the possibility for significant analytical variability between diverse types of materials and should plan to account for it. The degree of anticipated diversity, however, must be balanced against the costs of the additional duplicate analyses that are necessary to derive an adequate estimate of the analytical variation within each type. The final practical test is to determine whether the method of estimating the analytical-error variance affects the final interpretation of the overall study.

# ELEMENTS IN WHEATGRASS, DAVE JOHNSTON MINE by James A. Erdman and Richard J. Ebens

Crested wheatgrass was sampled on July 24, 1974, at the Dave Johnston mine as an adjunctive study to our main investigation of the compositional variability in sweetclover and spoil materials among surface coal mines of the Northern Great Plains (U.S. Geological Survey, 1975, p. 29-35). This grass dominates the revegetated spoil banks at the Dave Johnston mine, as it does at many of the surface mines that we sampled. According to James Sarvey of the mine staff (oral commun.), the intent is to eventually permit cattle to graze in the mined area; there was evidence even in 1974 that some cattle had already ranged over the reclaimed spoils.

Crested wheatgrass is of considerable value both as a reclamation plant and as a forage herb. It is used more widely for reseeding purposes than any other grass (Humphrey, 1960). Further, when actively-growing, there are few grasses that are more nutritious to livestock. When dry, however, its forage value is much less.

#### Methods

### Sampling design

Sampling was conducted according to a three-level analysis of variance design. The first level assessed the differences in element composition between wheatgrass growing on spoil materials and wheat-grass growing on comparatively normal soils. The second level estimated the degree of uniformity in the element composition of wheatgrass within these two substrate types. A third level, based on the analyses of splits of each sample, estimated the laboratory precision (reproducibility).

Ten sites were selected randomly from two tracts of reclaimed spoil piles; one sample of crested wheatgrass was collected from each site. We selected two sites from a 47-acre tract that had been seeded in the Fall of 1969 with a seed mixture that included Standard crested wheatgrass, Agropyron desertorum (Fisch.) Schult. The remaining eight samples were collected from sites in a 110-acre tract seeded in the Fall of 1972. The seed mixture in this latter tract included Fairway crested wheatgrass, A. cristatum (L.) Gaertn. Both tracts had been covered with topsoil to a depth of 4 to 6 inches (10-15 cm) in preparation for seeding, but the kind of surficial material at the sampling sites varied considerably, ranging from what appeared to be spoil material (mixed overburden and coal) to as much as ten inches (25 cm) of topsoil.

Our "control" samples were collected from two topsoil borrow areas, one seeded in the Spring of 1972 and totaling 30 acres; the other seeded in the Fall of that year and totaling 70 acres. Both areas were seeded with the Fairway species of wheatgrass. Inasmuch as only about six inches (15 cm) of the surface soil was removed and soils from the Powder River Basin tend not to vary chemically with depth (Tidball and Ebens, 1976), these ten samples seem adequate to provide valid baseline data.

Hanson and Churchill (1961, p. 92) described the two species of grass that we sampled as follows: "The Fairway strain of crested wheatgrass (Agropyron cristatum), much used in reseeding rangeland, is smaller, more decumbent, and finer-leaved than the Standard strain." Despite the morphological differences between the two species (or strains) of crested wheatgrass, our analyses indicated no clear element differences between the two.

The grasses we selected were clipped about 15 cm above the ground surface in order to minimize the effects of soil contamination. A composite sample of leaf and culm material was then placed in large cloth bags and taken to the U.S. Geological Survey laboratories in Denver, Colorado. Each sample was pulverized in a Wiley mill and the resulting homogenized material divided into two equal portions. The number of samples for this study was therefore doubled from 20 field samples to 40 laboratory samples. These 40 samples were then randomized before being submitted for chemical analysis. The analytical techniques used are given in U.S. Geological Survey (1975, p. 74-78). Analysts were T. F. Harms, C. S. E. Papp, and W. Cary.

#### Results and conclusions

We transformed all data to logarithms in order to better approximate normal frequency distributions for the element and ash analyses. Geometric means and deviations, therefore, are used as estimates of the most probable concentrations and of the degree of variability, respectively.

Results of the analysis of variance and appropriate summary statistics are given in table 11. Concentrations of six elements were significantly different (p <0.05) between crested wheatgrass samples taken from the spoil tracts and those taken from the topsoil borrow areas. Concentrations of Cd, Co, F, U, and Zn in samples that grew on spoils ranged from 140 to 400 percent higher than those grown on the borrow areas. Conversely, the P content in samples from the spoil tracts was about two-thirds that in the samples collected from the control areas. The analytical error for Hg, although extremely high when viewed as a percentage of the total variation, simply reflects the uniform concentration of this element in the sample material-ranging from 0.01 to 0.02 ppm. The error for Cd, too, is quite high when viewed as a percentage and reflects a similar compositional uniformity in the data from each area. The non-laboratory variation in Cd appears to reflect solely a "treatment" effect.

Where the detection ratio is less than one, means and variance were estimated by techniques developed by Cohen (1959) and described in mathematical detail for geochemical applications by Miesch (1967). Because the analysis of variance requires a completely numeric data set, we arbitrarily assigned small values equal to 0.7 of the limit of detection of a given element to samples whose concentration was too low to be measured.

Table 11.-- Statistical analysis of element concentrations in the ash of crested wheatgrass from topsoil borrow areas and from reclaimed spoil areas at the Dave Johnston Wine, southern Powder diver Dasin, Woming

Concentrations expressed as parts per million, except for Ca, Na, K, P, S, Si, and ash, which are in percent; \*, component of variance tested to be significant at the 0.05 probability level; ratio, number of samples in thich element was detected to total number of samples analyzed.

		Ans	Analysis of variance	rriance			U	Summary statistics	istics			
í	Total	Later I	l L	Variance		Topsoil	borrow	areas		Reclaimed	ed spoil areas	Sec
Element or ash	log10 variance	Between areas	creas	que to analytical error	Katio	Geometric mean	Geometric deviation	Observed renge	Ratio	Geoma <b>tric</b> mean	Goometric deviation	Observed range
20 C	95,00*0	7	۵. **	ν.	20:20	T•17	1.11	3.6-5.2	20:20	3.9	1,21	2.5-5.3
Cd	.0702	*12	<b>ば</b> >	73	20:20	•86	1.90	.2-2	20:20	7.1	1.40	.6-2
00	1650	35*	13	52	10:20	.72	1.76	<1-5	15:20	1.5	2.59	<1-8
F2/	.0240	30*	61*	6	20: 20	4.5	1.17	3-6	20:20	6.2	1,46	3-10
Ë 3/	.0138	Ç	18	82	20:50	10.	1.33	.0102	20:20	1.10.	1.29	.0102
K	8410.	ť,	. *96	7	20:20	18	1.23	13-24	20:20	50	1.38	9.8-30
	1601.	15	83*	2	20:20	13	2.02	4-30	20:20	22	1.93	8-65
e)	1990*	۲,	*48	13	15:20	.27	2,32	<.28	18:20	.37	1.67	<.28
	.0267	555*	29*	16	20:20	2.1	1.16	1.8-2.4	20:20	1.1	1.38	.6-2.4
S, total 2/	.0203	۲,	*16	m	20:20	.17	1.29	.1027	20:20	.18	1.45	.0933
Se2/	.0710	₽	81%	6	20:20	.23	1.91	.1060	20:20	.27	1.73	.1070
Si	.0138	15	65*	50	20:20	50	1.22	14-26	20:20	16	1.33	9-4-26
U	.2165	39*	*175	7	9:20	.25	८•्म	<-li>1-1.2	19:20	1.0	3.02	<-h-10
Zn	•010	*65	39*	<b>2</b>	20:20	310	1.20	220-460	20:20	०ग्	1.25	300-580
Ash	.0035	۲ ۲	*176	9	20:20	6.3	1.15	5.3-8.0	20:20	0.9	1.1	2.6-5.3
		-	-designations in the content of the		THE PERSON NAMED IN COLUMN TWO IS NOT THE OWNER.	-				-		

 $\frac{1}{2}$  increased as percent of the total variance 2 Analyses determined on dry material, not ash; therefore expressed on dry-weight basis.

Two additional elements of great environmental interest but for which only very limited data are available are Sb and As. Their detection ratios and ranges in ppm follow: Sb, 0:40, <0.05; As in wheatgrass from the topsoil borrow areas, 1:20, <0.05-0.05, and in wheatgrass from the reclaimed spoil areas, 10:20, <0.05-0.09.

It is clear from these results that a substrate of reclaimed spoil material can affect the trace element chemistry of crested wheatgrass. The next and more difficult step is to assess these changes as they might apply to productive post-mining land use. How will these geochemical alterations affect the nutritional requirements of range plants or of livestock that utilizes the forage?

Possible deficiencies in elements essential to vegetation have attracted a major interest in mine-spoil reclamation efforts. One such essential element is phosphorus. Our analyses of P in crested wheatgrass confirms the conclusions of Sandoval and others (1973) that the available P in spoil materials derived from the Fort Union Formation is generally very low, and is the most pronounced fertility limitation to successful revegetation of reclaimed spoil banks. The fact that wheatgrass is reasonably well-established at the Dave Johnston mine, however, is evidence that these limitations are not insurmountable.

The problem of potentially toxic elements is more intractable. The slight but significant increases in Co and Zn in the spoil-associated wheatgrass may be of little consequence, for most problems associated with these elements have involved deficiency diseases in livestock (Lee, 1975). Significant increases in Cd and F were also noted for those samples that grew on spoil material. There is some indication that acid spoils promote fluoride uptake in plants (National Research Council, Committee on Animal Nutrition, Subcommittee on Fluorosis, 1974), and the pH of the spoils that we sampled (this report, table 1, pH = 6.2at Dave Johnston mine) is, on the average, considerably lower than the pH of 7.2, typical of the surface horizon of the Powder River Basin soils (U.S. Geological Survey, 1975, p. 27). This may account, at least in part, for the significant F effect. The toxicity of Cd and F to livestock is well known. Chronic fluorosis in grazing animals, recognized as a disease entity in 1931, has been widely encountered throughout the However, the F concentrations in all samples of crested wheatgrass from the Dave Johnston mine were well below levels at which normal performance in livestock may be affected; natural forage normally contains 2 to 20 ppm F on a dry-weight basis (National Research Council, Committee on Animal Nutrition, Subcommittee on Fluorosis, 1974). The Cd concentrations also appear normal when compared with ranges found in other native plants (Connor and Shacklette, 1975). As for U, we know of no recognized critical levels in forage, either from a radiation or chemical viewpoint.

## GEOCHEMISTRY OF GROUND WATERS IN THE FORT UNION COAL REGION by Gerald L. Feder and Lynda G. Saindon

Since the last progress report all laboratory analyses for the samples collected in the Fort Union coal region have been completed and statistical analysis of the data has been performed and is presented herein.

### Sampling design

Field sampling in the Fort Union coal region was based on a Stage la nested analysis-of-variance sampling plan (Miesch, 1976), according to the model:

$$log X_{ijk} = M + T_i + S_{ij} + E_{ijk}$$
,

where the logarithm of the concentration of a chemical constituent for a given ground-water sample, as reported by the analyst (log  $X_{ijk}$ ), is assumed to deviate from the true logarithmic average for that material (M) by the cumulative effect of three independent sources of variation. T, represents broad scale differences observed between townships within the Fort Union coal region,  $S_{ij}$  represents differences between wells spaced within 5 km of each other, and  $E_{ijk}$  represents ever-present nongeographic effects, including errors caused by sample collection, shipping procedures, and laboratory methods (analytical errors). These last effects are estimated independently by obtaining duplicate samples at randomly selected wells and analyzing them in random order. Estimates of the variance of the above effects, denoted as  $S_1^2$ ,  $S_2^2$ , and  $S_i^2$ , respectively, can be computed using procedures given in Anderson and Bancroft (1972, p. 327), and their sum ( $S_{ijk}^2$  y) represents the total observed logarithmic variance in the study area. The study in the Fort Union coal region is part of a larger study--that of ground-water chemistry in all of the western coal region. In this context, the above equation could be expanded to include a regional effect,  $S_R^2$ , which would reflect differences among coal regions in the Rocky Mountain and Northern Great Plains Provinces.

Estimates of  $S_T^2$  have been obtained from samples of wells in each of 19 randomly selected areas (townships) within the study area (see fig. 28). In order to estimate  $S_S^2$ , 4 of these areas were randomly chosen, and an additional well within 5 km was sampled.

All samples were collected from geologic formations above the Pierre Shale, including glacial drift, and only wells used for human or livestock water supplies were chosen, regardless of depth. The average well depth is about 30 m.

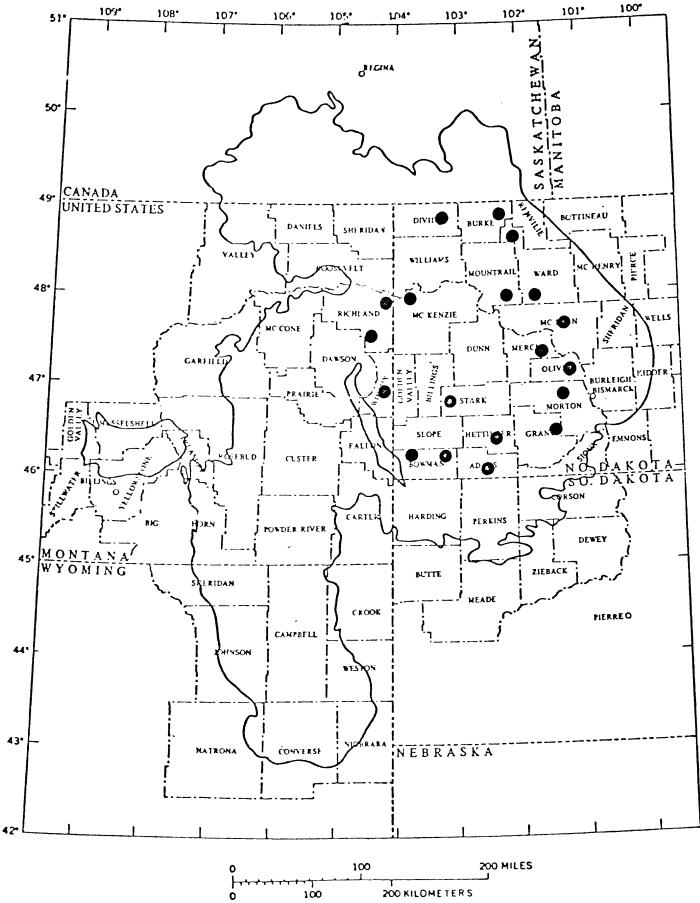


Figure 28. Locations selected for sampling well water in the Northern Great Plains Coal Region.

Chemical variability of ground water in the Fort Union coal region

Results of an analysis of variance of data from ground-water samples from the Fort Union coal region indicate that for most of the chemical constituents analyzed, most of the variance is large scale, that is between widely spaced sampling sites within the region (see table 12).

In addition, because of the large values for the variance of most chemical constituents the confidence with which one could predict the chemical composition of a randomly selected well in the region would be poor. Recent work by Thorstenson, Fisher, and Croft (oral commun., 1976) has helped to explain at least part of the high variability of many chemical constituents. In the Fox Hills aquifer of the Fort Union coal region, Thorstenson and colleagues have found that as ground water moves downdip from recharge areas a combination of chemical reactions with the aquifer minerals, sulfate reducing bacteria, and exchange reactions with aquifer clays, gradually change the water from a Ca Mg + HCO 3SO 4 type that has a pH around 8.0, to a  $Na^{+}HCO_{3}^{-}$  water that has a pH above 8.5. Even though ground waters near the recharge areas may contain appreciable Na and HCO3, the deeper waters contain much higher Na and HCO3 concentrations. Constituent correlation coefficients based on data from the 19 randomly selected wells of this study in general support the process as described by Thorstenson and colleagues. For example, Na, pH, HCO3, and total dissolved solids (TDS) tend to increase together, while SO4, Ca, Mg tend to decrease in relation to these constituents, as shown in the following table:

	Log Na	$Log\ HCO_3$	Log TDS	Log SO <sub>4</sub>	Log Ca	Log Mg
pH Log Na	0.40	0.47 .84	-0.04 .79	-0.43 .16	-0.88 .46	-0.83 45
Log HCO <sub>3</sub>			.51	09	<b></b> 56	53
Log TDS				.55	<01	.01
Log SO <sub>4</sub>					.55	.62
Log Ca						.95

The positive correlation between  $SO_4$  and TDS is a result of some recharge area ground waters having relatively high TDS with  $SO_4$  as the major anion. Such waters would show an increase in dissolved solids and a reduction in sulfate as the water moved down gradient. In contrast, ground water from recharge areas that starts with relatively low dissolved solids might end up down gradient with a dissolved solid content lower than some recharge area waters. In both cases, however, there is a reduction in sulfate and an increase in dissolved solids downdip.

From the small number of samples collected in this study, it appears that the scale of this process is not regional, or basin wide, but rather is on a scale of less than 100 km. In addition the initial compositions of ground waters in the recharge areas further obscure this process. However, ratios of the various chemical constituents in recharge areas

Table 12. -- Analysis of logarithmic variance for ground waters of

the Fort Union Formation, North Dakota and Montana.

[An asterisk (\*) indicates component is significantly different from zero at the 0.05 probability level; data in milligrams per liter, except where noted as picocuries per liter (pCi/1) or micrograms per liter ( $\mu$ gm/1)]

		Varianc	e component	(%)
Constituent	Total Log <sub>10</sub> variance	Between areas	Between wells	Between samples
Ra (pCi/1)	0.242	41.8	56.6*	1.5
U (μg/1)	.979	96.5*	2.6	.8
β (pCi/1 as Sr/Y-90)	.097	87.6*	.0	12.4
TDS mg/1	.066	82.5*	17.4*	<.1
рН	$.375^{1/}$	96.8*	3.2	<.1
Temperature (°C)	.011	81.4*	18.6	<.1
HCO <sub>3</sub> (mg/1)	.039	82.8*	17.2*	<.1
Br (mg/1)	.171	86.7*	4.4	8.8
Ca (mg/1)	.484	98.8*	1.2*	<.1
C1 (mg/1)	.232	99.0*	.5	.4
Hardness (Total as CaCO <sub>3</sub> ) mg/1	.546	98.6*	1.2*	.1
Mg (mg/1)	.715	98.3*	1.3	.3
Mn (µg/1)	.340	89.8*	7.8	2.4
K (mg/1)	.095	85.6*	14.2*	.2
$SAR^{2}$	.485	97.9*	2.1	<.1
SiO <sub>2</sub> (mg/1)	.042	99.5*	.0	.4
Na (mg/1)	.192	90.5*	9.4*	.1
SO <sub>4</sub> (mg/1)	.504	81.8*	18.2*	<.1
Zn (µg/1)	.578	45.7	54.1*	.1
A1 (μg/1)	.124	44.6	25.8	29.5
Ba (µg/1)	.171	85.0*	14.0*	.9
B (μg/1)	.168	64.4	35 <i>.</i> 1*	.5
Li (11 g/1)	.062	59.4	32.2	8.4
Sr (µg/1)	.160	85.0*	10.4	4.6
Fe (u g/1)	.313	75.3	24.0*	.7

<sup>1/</sup> Measured in standard units.

<sup>2/</sup> Sodium absorption ratio.

are generally much less variable than the individual chemical constituents. For example, despite high variability of Na content of ground water from recharge areas, the sodium absorption ratio (SAR)— in recharge areas is

$$\_/ SAR = \sqrt{\frac{Na}{\frac{Ca+Mg}{2}}}$$

generally less than 5, while in downdip ground waters it reaches values as high as 86. This latter point may have important implications for coal spoil-pile reclamation and irrigation, and indicates the wide range in suitability of ground water for such uses.

As shown in table 13, in addition to large variations in the concentrations of major elements, most trace elements also show wide variations. The large variability in the trace-element concentrations of the ground waters is controlled in many instances by the same geochemical processes controlling the concentrations of major chemical constituents. For example, as the sulfate is reduced by sulfate reducing bacteria to  $H_2S$ , the  $H_2S$  in turn precipitates the trace metals, greatly lowering their concentration in the ground water. Waters which have a reducing potential due to production of  $H_2S$  can also control the solubility of uranium.

Despite the large variations in trace element concentrations in the ground waters of this region, only a few samples show trace element concentrations above maximum contaminant levels established by the safe drinking water act (U.S. Environmental Protection Agency, 1975; 1976), as outlined below. Those trace elements involved include fluorine and gross  $\alpha$ .

Constituents	Maximum allowable values	Constituents	Maximum allowable values
As	0.05 mg/1	NO <sub>3</sub> (as N)	10.0 mg/1
Ва	1.0 mg/1	Se	.01 mg/1
Cđ	.01 mg/1	Ag	.05 mg/1
Cr	.05 mg/1	F	1.4-2.4 mg/1*
Pb	.05 mg/1	Gross alpha	15 pCi/1
Hg	.002  mg/1	Gross beta	50 pCi/1
-	_	<sup>Ra</sup> 226,228	5 pCi/1

<sup>\*,</sup> varies with annual average of the maximum daily air temperature for the locality.

Table 13.--Geochemical summary of ground water from the Fort Union Formation,

North Dakota and Montana

[Data expressed as milligrams per liter except where noted as micromhos per centimeter (µ mhos/cm), micrograms per liter (µ gm/1) and picocuries per liter (pCi/1); detection ratio is number of samples in which constituent was determined to total number of samples analyzed]

	Detection ratio	Geometric mean	Geometric deviation	Maximum	Minimum
Sp. Cond. (µmhos/cm)	19/19	1690	1.66	4300	495
Diss Solids (180°C mg/1)	19/19	1031	1.92	4140	281
рН	<b>19/1</b> 9	7.8 $\frac{1}{}$	$.64^{1/2}$	8.89	6.55
<b>Temper</b> ature °C	19/19	9.6	1.27	20.4	7.1
Alkalinity (mg/1)	19/19	576	1.60	1070	206
A1 (µg/1)	18/19	24	2.36	90	<5
As (μg/1)	9/19	<1		<b>2</b> 6	<1
Ba (μg/1)	19/19	50	2.58	520	13
Be (4g/1)	0/19	<7			
HCO <sub>3</sub> (mg/1)	19/19	665	1.63	1160	251
Bi (µg/1)	0/19	<14			
B (μg/1)	19/19	175	2.72	800	23
Br (mg/1)	15/19	.21	2.87	1.7	<.1
Cd (µg/1)	2/19	<1		1	<1
Ca (mg/1)	19/19	28	4.50	<b>3</b> 50	1.8
C1 (mg/1)	19/19	15	<b>3.4</b> 5	170	1.8
Co (µg/1)	0/19	<14			
Cu (µg/1)	8/19	<1		15	<1
Cr (µg/1)	0/19	<14			
F (mg/1)	19/19	.6	3.19	7.5	.1
Ga (µg/1)	0/19	<2			
Ge (µg/1)	0/19	<15			
Hardness (Total as CaCO <sub>3</sub> mg/l)	19/19	126	4.98	1900	5
Hardness (non-carb mg/1)	6/19	<1		1600	<1
I (mg/1)	8/19	<.01		.78	<.01

Table 13.--Geochemical summary of ground water from the Fort Union Formation,

North Dakota and Montana--Continued.

		Detection	Geometric	Geometric	Wassian	V4 4
		ratio	mean	deviation	Maximum	Minimum
Fe	(μg/1)	19/19	427	3.88	5000	70
РЪ	(μg/1)	0/19	<14	<b>~~</b>		~ ~
Li	(μg/1)	19/19	49	1.79	150	20
1g	(mg/1)	18/19	12	6.73	240	<.1
<b>í</b> n	(μg/1)	15/19	31	3.73	470	<1
łg	$(\mu g/1)$	4/19	<.1		.1	<.1
10	(µg/1)	7/19	<1		30	<1
li	(μg/1)	0/19	<14			~~
ζ	(mg/1)	19/19	4.6	1.77	34	1.5
Se	(u g/1)	6/19	<1		6	<1
SiO <sub>2</sub>	(mg/1)	19/19	14	1.61	27	6.2
Ag	(µg/1)	0/19	<3			
Na	(mg/1)	19/19	219	2.97	760	23
SAR <sup>2</sup> /		19/19	8.5	5.08	86	.7
SO <sub>4</sub>	(mg/1)	19/19	128	5.12	2400	4.7
Sn	(µg/1)	0/19	<18			
Sr	(µg/1)	19/19	551	2.40	3800	110
Γi	(ug/1)	1/19	<2		150	<2
1	(µg/1)	0/19	<14		dia dia	
Zn	(µg/1)	16/19	42	6.58	1600	<10
Zr	(ug/1)	0/19	<b>&lt;2</b> 5			
Gross	alpha ( $\mu$ g/1 as u-nat)	4/19	<4.2		49	<4.2
Gross	beta (pCi/1 as Sr/Y-90)	15/19	5.7	1.87	22	<2.9
Radiu	m <sub>226</sub> (pCi/1)	16/19	.40	3.12	4.2	<.1
Jrani	um (µg/1)	18/19	.74	12.5	40	<.01

 $<sup>\</sup>underline{1}/$  Arithmetic mean and standard deviation.

<sup>2/</sup> Sodium absorption ratio.

## Comparison of use of 0.45-micrometer filter with 0.10-micrometer filter

By convention a 0.45-micrometer filter is normally used to filter water samples in the field. However, Kennedy, Zellweger, and Jones (1974) and U.S. Geological Survey (1972, p. 81) have shown that for some samples a 0.45-micrometer filter allows appreciable fine particulate material to pass through the filter, which may significantly affect the resulting chemical analysis. When the water-quality data obtained in this manner are interpreted as dissolved chemical constituents, large errors may result in the interpretation due to variations in the quantity of particulate material passing through the filter. The above investigators found that using a 0.10-micrometer filter greatly reduced the amount of fine particulate material passing through the filter, and resulted in water-quality data that more accurately defined soluble constituents. The chemical constituents studied also more closely approached their calculated thermodynamic solubilities.

A test was run to determine if using a 0.10-micrometer filter rather than a 0.45-micrometer filter would have a significant effect on analytical results obtained for ground waters from the Fort Union coal region. At each of three random sites where duplicate samples were collected using a 0.45-micrometer filter, a third sample was also collected using a 0.10-micrometer filter. Results of this experiment indicate no recognizable difference between laboratory results obtained for the two 0.45-micrometer filtered samples and the 0.10-micrometer filtered sample. The differences found appear to lie within the limits of analytical precision for each of the chemical constituents analyzed. In addition to the results obtained from comparison of the 0.1 and 0.45micrometer data, all the other laboratory data show expected low concentrations of insoluble chemical constituents, which indicates insignificant effects on analytical results by particulate matter. The only exception to this conclusion was the measurement of unusually high concentrations of Ti in two closely-spaced wells. These wells will be resampled. We cautiously conclude, therefore, that for most ground-water sampling in the Northern Great Plains Coal Province a 0.45-micrometer filter is sufficient. However, if much fine sediment is encountered in a groundwater sample, or if anomalously high concentrations of relatively insoluble chemical constituents such as aluminum or titanium are obtained, a 0.10-micrometer filter should be used.

# GEOCHEMISTRY OF THE FORT UNION FORMATION by Richard J. Ebens and James M. McNeal

#### Introduction

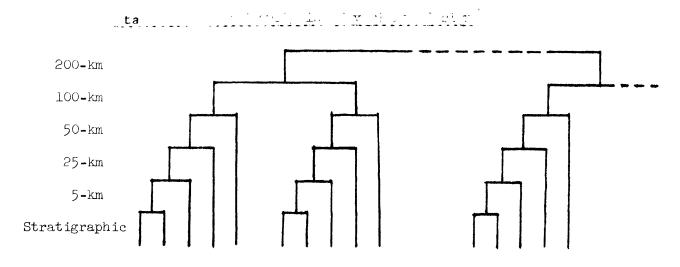
The Northern Great Plains Coal Province includes the lignite deposits in the Northern Great Plains of eastern Montana and western North Dakota and South Dakota as well as the coal deposits in the Powder River Basin of northeastern Wyoming and southeastern Montana. Most of the strippable coal beds in this region are in the Paleocene Fort Union Formation. This formation consists of interbedded siltstone, claystone, and sandstone deposited in a deltaic floodplain-floodbasin environment. Any substitution, even partial, of these overburden rock materials for natural soils in areas of strip mining, may cause substantial changes in the chemical composition of the surface environment in these disturbed areas. A knowledge of the geochemistry of potential overburden rock materials may indicate which, if any, of these materials could be substituted for soil with minimal chemical change.

To acquire this knowledge, a suite of shale and sandstone samples was collected from outcrops of the Fort Union Formation throughout the Northern Great Plains Coal Province during the summer of 1975. This initial reconnaissance study was undertaken to assess the magnitude and distribution of chemical variation in these rock units. The purpose of this report is to describe the sampling design and to present some preliminary results of the study.

### Sampling design and analytical procedures

Samples for this study were collected according to a staggered nested analysis of variance design (Leone and others, 1968). The sampling design, which is outlined below, has five geographic "levels", one stratigraphic "level" and a "level" of laboratory error. Sampling localities are shown in figure 29 and consist of a randomly selected outcrop of the Fort Union Formation within a 5-km cell. At 10 of the 40 localities shown, two samples of each rock type (shale and sandstone) were collected from a stratigraphic section in order to estimate stratigraphic variability. Geographic variability was estimated by nesting 5-km cells within 25-km cells, 25-km cells within 50-km cells, 50-km cells within 100-km cells, and 100-km cells within 200-km cells. Laboratory error was estimated by splitting 20 of the 60 samples into two parts resulting in a total analytical load of 80.

The two sample groups, shale and sandstone, were each submitted to the laboratories in randomized sequence. Each sample was crushed in a jaw crusher and then ground in a vertical Braun pulverizer with ceramic plates set to pass 100 mesh. T. L. Yager analyzed the samples for total carbon, J. G. Crock analyzed for zinc, and W. Mountjoy analyzed for magnesium, sodium, lithium, and rubidium. Methods used for analyzing for these elements are described in U.S. Geological Survey (1975, p. 71-73).



		Number of units	Degrees of	
Level	Source of variation	at each level	freedom	
- 1	Between 200-km cells	6	5	
2	Between 100-km cells	12	6	
3	Between 50-km cells	24	12	
4	Between 25-km cells	36	12	
5	Between 5-km cells	48	12	
6	Stratigraphic	60	12	
7	Laboratory	80	20	

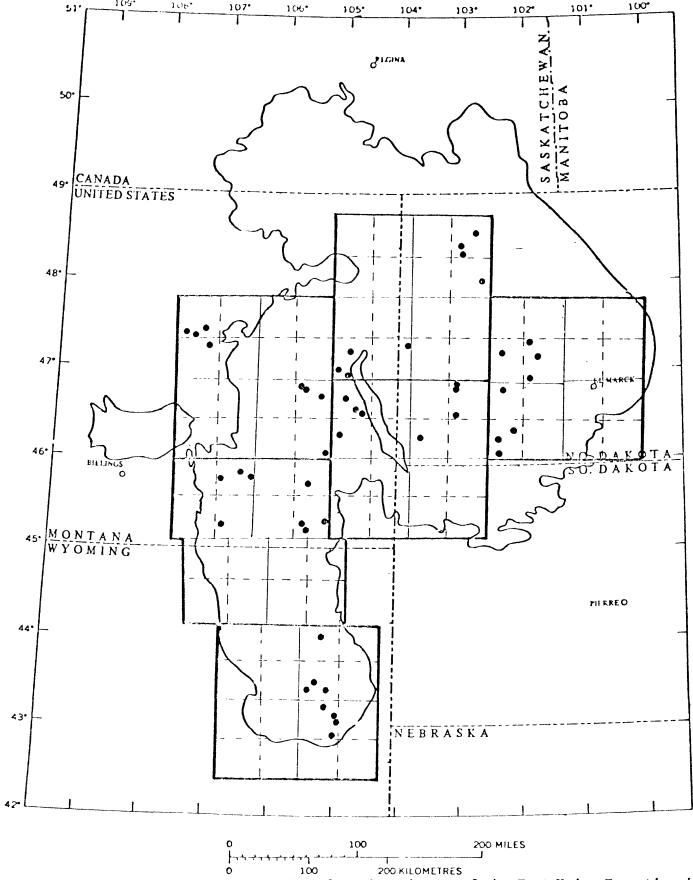


Figure 29.--Sampling localities of shale and sandstone of the Fort Union Formation in the Northern Great Plains Coal Province. Large squares are 200 km on a side; intermediate squares, 100 km; and smaller squares, 50 km. Dots indicate sampling localities. Map adapted from U.S. Geological Survey (1974a) and Whitaker and Pearson (1972).

#### Geochemical variation

Variance components and summary statistics for six elements in shale and sandstone are given in table 14. In shale, most of the variation occurs at local scales (within 25-km cells) except for sodium which has important regional variation. In contrast, four elements (total carbon, sodium, magnesium, and zinc) of the six in sandstone have important regional variation. The regional differences in sandstone are probably related to differences in feldspar and dolomite concentrations. However, quantitative mineralogical work (X-ray diffraction work) has not been completed on these sample suites and until completed, we can only speculate as to the cause of these differences.

# Geochemical maps

The variance mean ratio,  $v_m$ , (Miesch, 1976) was calculated to determine the feasibility of mapping those elements that have significant variation among 200-km cells. This ratio, given in table 14, is an index of the stability of a map pattern. A ratio of one or greater indicates that differences among 200-km cells means are stable at the 80-percent confidence level. Maps of sodium in shale and total carbon, sodium and magnesium in sandstone are judged to be stable and appear in figures 30-31.

The exceptionally low values noted for  $Na_2O$  in both shale and sandstone collected from outcrops in the southeastern Powder River Basin are clearly anomalous compared to Fort Union Formation samples elsewhere, and very likely indicate a general lack of feldspar. Similarly, the low content of MgO in outcrops of sandstone throughout the southern part of the study area (including the Powder River Basin) probably reflects more abundant dolomitic cement in the northern outcrops. The regional distribution of total carbon in sandstone varies by a factor of about 3.0 (fig. 31) but is a more erratic pattern than are those of  $Na_2O$  or MgO. The lack of a pattern for total carbon similar to that for MgO indicates that the southern outcrops are more carbonaceous than the northern outcrops.

Table 14. Statistical analysis of the chemistry of shale and sandstone of the Fort Union Formation, Northern Great Plains Coal Province

 $[\star, \,$  significantly greater than zero at the 0.05 probability level]

			Analysis	of logar	Analysis of logarithmic variance	rlance							
1				Percent of	of total	total variance			/ī ·		Summary statistics	atistics	
	Total Log <sub>10</sub>	Between 200-km	Between 100-km	Between Be 50-km 25	Between 25-km	Between 5-km	Strati-	Labora-	(200-km	Geometric	Geometric	Geometric	Expected 95 percent
Constituent	Variance	cells	cells	cells	cells	cells	graphic	tory	cells)	mean	deviation	error	range (baseline)
							Shale						
C, total, %	0.2699	< 1	大1	2	< 1	29	36	23	0	96.0	3,31	1.77	0.11-77
L1, ppm	.0631	۷ ۲	17	<b>^</b> 1	1	78*	Å	2	0	31	1.78	1.09	6.9-97
Mgo, 7	.1538	*	ω	8	۰ ا	<b>70</b> *	13	۷ 1	ω.	2.4	2.47	< 1.09	1
Na20, Z	.1620	38	۷ ۲	-	20	28*	ð	2	1.6	. 58	2,53	1.14	
Rb, ppm	.0708	m	19	<b>1 &gt;</b> 1	۷ ا	\$	ž.	<b>^</b> 1	.2	110	1.85	< 1.06	32-370
Zu, ppm	.0726	<b>1</b> >	, 1	35	1 >	<b>45</b> *	5 <u>%</u>	\ \	0	80	1.86	< 1.06	23-270
							Sandstone						
C, total, 7	.5679	32*	21*	<b>,</b>	14	11	13	σ.	1.2	1.0	5.67	1.68	1 1 1 1
Li, ppm	.0186	۷ ۱	۷ ۲	***	m	23	58	н	0	15	1.37	1.03	8.0-28
Mgo, %	.2482	*Z7	20*	<b>,</b>	18*	1	18	\ 1	1.8	1.7	3,15	< 1.12	1
Na20, %	1914	\$05	< 1 ×	22	< 1 ×	264	*		1.9	.67	2.74	1,11	
Rb, ppm	.0178	۸ ،	, ,	36*	<b>^</b> 1	3&	26*	2	0	59	1,36	1.04	32-110
Zu, ppm	.0463	24*	<b>^</b> 1	344	å	σ.	1	23	۲.	43	1.64	1.27	# 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
			-		-			***************************************	***************************************				

1/ Variance mean ratio for 200-km cells. See text for explanation.

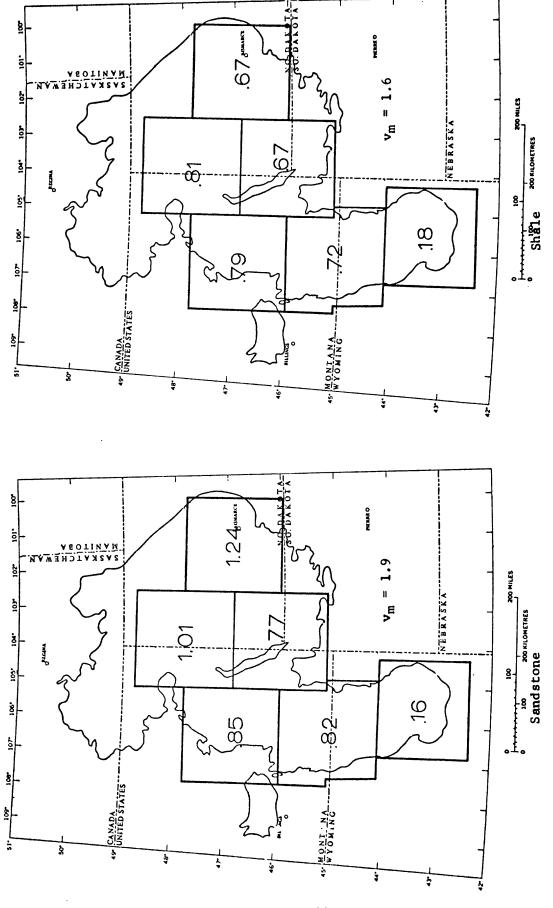


Figure 30. --Regional distribution of Na20 in sandstone and shale of the Fort Union Formation. Values v<sub>m</sub> is index of stability. are means (in percent) of 200-km cells.

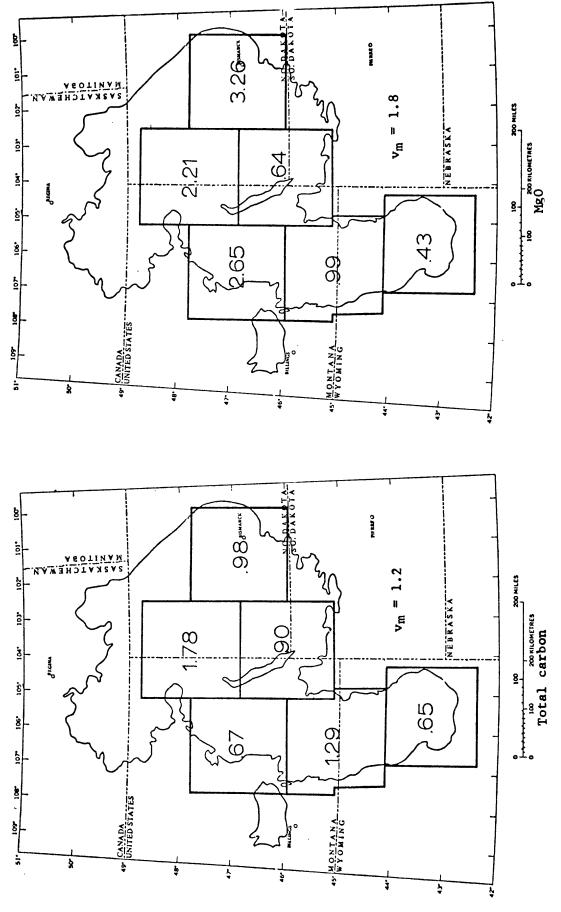


Figure 31.--Regional distribution of total carbon and MgO in sandstone of the Fort Union Formation. Values are means (in percent) of 200-km cells. vm is index of stability.

SOIL CHEMISTRY IN THE PICEANCE CREEK BASIN by Charles D. Ringrose\_, Ronald W. Klusman\_, and Walter E. Dean

#### Introduction

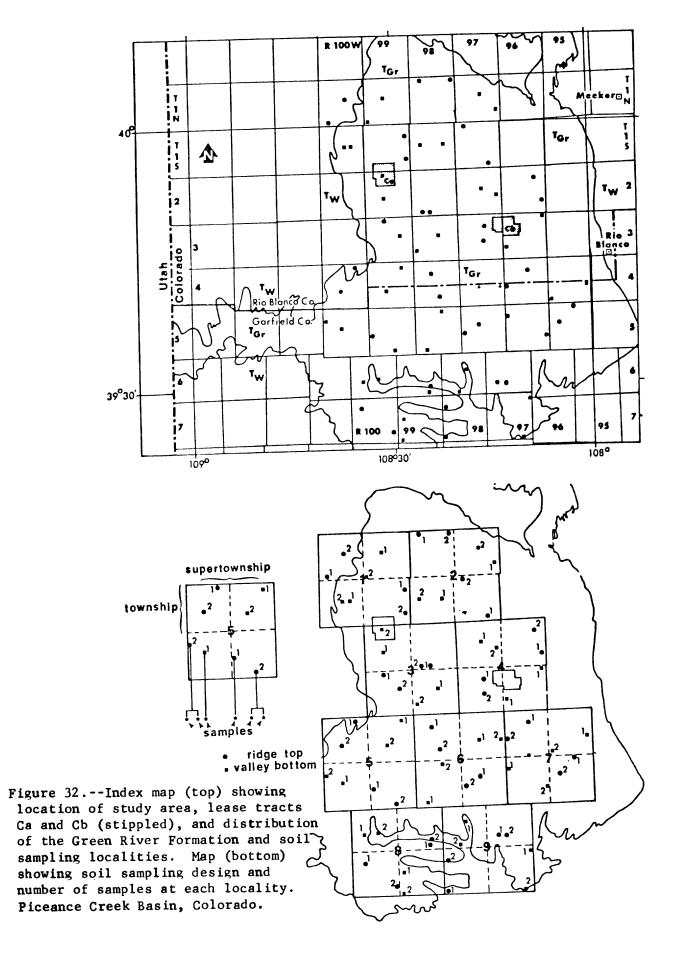
The oil-shale regions of Colorado, Wyoming and Utah hold promise of providing a substantial amount of liquid hydrocarbons within the next decade, and environmental baselines for soil, plant, air, and water quality are needed prior to economic development. An important part of this need is the establishment of trace-element baselines in surficial materials. A knowledge of the variance of trace-element concentrations, in particular, would allow the determination of the soil sampling interval required in order to construct practical geochemical baselines in this and adjacent areas.

The main objective of this study was to establish the extent and magnitude of regional variations in major and trace elements in soils within the Piceance Creek Basin of western Colorado. The sampling design was constructed to test geochemical variability at a number of geographic levels (distances between samples) as well as at one physiographic level (ridge top vs. valley bottom). A secondary goal was to provide a first approximation of natural (baseline) variations in soil composition within the Piceance Creek Basin, and to provide a scale for measuring deviations from the baseline during the course of oil shale production, processing, and land reclamation. R. J. Ebens and R. R. Tidball provided valuable assistance with the sampling design. A. T. Miesch and R. R. Tidball helped with the statistical analyses. We extend special thanks to J. G. Boerngen who did most of the data processing.

### Sampling design

The sampling design for the study of soils in the Piceance Creek Basin is a partially unbalanced nested analysis of variance design. The sampling localities are shown diagrammatically in figure 32. The initial sampling design, as used in the field, was balanced. Within each of 36 townships, 2 sections were chosen at random. Within each section, two samples of surface soil were collected 100 meters apart. All four samples within a given township were collected either from ridge tops or valley bottoms. Ridge top and valley bottom sampling alternated according to a checkerboard design. By eliminating one sample from one section in each township, a slightly unbalanced design resulted in a reduction of analytical load of 25 percent. The decision as to which of the two sections in each township would have two samples included in the analytical design, and which would have only one was made by a simple flip-of-the-coin. This technique was also used to decide which of the samples to eliminate in the section chosen for only one sample. A higher geographic level was constructed by grouping all

\_/ Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colo.



samples within four adjacent townships into a "supertownship". From the 108 samples used in this design, 32 were chosen at random to be replicated in analysis. The final design therefore consisted of six levels -- one physiographic (ridge top vs. valley bottom), four geographic (between supertownships, between townships, between sections, and between samples, and one analytical (32 replicate analyses). All 140 samples (108 separate samples plus 32 replicates) were submitted for analysis in a randomized sequence. Level 1 (the top level) was designed to examine geochemical differences between soils on ridge tops and those in valley bottoms, level 2 was designed to examine geochemical differences at geographic scales greater than 19 km (between supertownships), level 3 examines differences at scales from 3 to 19 km (between townships), level 4 examines differences at scales from 0.1 to 3 km (between sections), and level 5 examines differences at a scale of 100 m (between samples). Level 6 measures analytical precision and includes errors due to sample inhomogeneity, sample preparation, and analysis.

# Chemical analyses

The samples were ground with a ceramic mill to pass a 100-mesh sieve. The major elements A1, Si, Ca, Ti, Fe, and K, and the trace elements Sn, Sb, Ge, As, and Se were analyzed by X-ray fluorescence by J. S. Wahlberg, Michele Goff, and J. W. Baker. Violet Merritt and Wayne Mountjoy analyzed the samples for Mg, Na, Li, and Rb by atomic absorption spectrometry. Atomic absorption was also used by J. G. Crock and G. O. Riddle to determine Zn concentrations. Johnnie Gardner and Patricia Guest determined F using the specific fluoride ion electrode method. Mercury was determined by the wet oxidation, flameless atomic absorption method by J. A. Thomas and G. O. Riddle. Total carbon was determined by combustion by V. E. Shaw. The remaining trace elements (B, Ba, Be, Co, Cr, Cu, Ga, Mn, Mo, Nb, Ni, Pb, Sc, Sr, V, Y, Yb, and Zr) were all determined by plate-reader optical emission spectrometry by Arthur L. Sutton and Richard Lemert. Details of these analytical methods are described in U.S. Geological Survey (1975, p. 69-81, and this report, p.

# Results

Logarithmic variance components for 37 elements in soils from Piceance Creek Basin (table 15) shows that most of the geographic variation for most elements occurs between sections (0.1 to 3 km). This conclusion supports analysis of variance results for soils from other areas which indicate that most of the variability in soil composition occurs at local scales (U.S. Geological Survey, 1975, p. 20-28, 36-49).

Of the 37 elements listed in table 15, 27 have significant variance components at the section level (A1, Ca, Fe, Mg, K, Si, Na, Ti, As, B, Ba, Be, Co, Cr, Cu, Ga, Hg, Li, Mo, Pb, Rb, Sc, Sr, V, Y, Yb, and Zn).

Table 15. -- Analysis of variance of surface soil chemistry, Piceance Creek Basin, Colorado [\*, indicates component is significantly different from zero at the 0.05 probability level]

		Variance	components	as percenta	ge of total	variance	
		Between	Between	<b>5</b>	7	<b>D</b>	
	Total	Ridge Tops and	Super-	Between Townships	Between Sections	Between Samples	Analytica: Error
Element	Logarithmic Variance	Valley Bottoms	(>19 km)	(3-19 km)	(0.1-3  km)	(0-100 m)	EFFOF
	0.0044		18	0	58*	14*	10
Al Ca	.1596	0	28*	15*	48*		0
Fe .	.0080	ő	27*	10	38*	9 2	33
Mg	.0291	Ö	28*	3	57*	ī	33 11
K	.0075	2	7	0	80*	6*	5 10
Si	.0038	0	22*	, 0	46*	22*	10
Na	.0473	0	4	41*	46*	6 <b>*</b>	3 8
Ti	.0064	1	28 <b>*</b> 14	0 26*	54*	9*	10
Total-C	.0535	1	14	20*	19	31*	10
As	.0914	0	0	0	81*	6	13
В	.0173	0	18*	0	57*	5 6	21
Ba	.0313	0	0	0	35*	6	58
Be	.0264	0	24* 12	0	37*	0	39
Co Cr	.0452	0	17*	0	33* 37*	0	75
Cu	.0821		28*	ő	18*	ĭ	52
F	.0331	0 3 0	7	0	15	34*	41
Ga	.0677	Ō	10*	0	59*	0	13 21 58 39 55 46 52 41 32 61 75 88 33 82
Ge	.1378	0 2	0	11	0	27 4	62
Hg	.1631	2	10	36*	31* 58*	10*	17
Li Mn	.0363	5	23 <b>*</b> 0	0 8	50° 4	0	88
Mo	.0976	ő	11	ő	48*	ž	33
Nb	.1055	0	1	0	17	Ó	82
Ni	.0694	0	10	0	24	36*	30
Pb	.1029	0	6	0	39*	0	55
Rb	.0127	0 1	0	0	77 <b>*</b> 0	6 <b>1</b> 0	86
Sb Sc	.0491	0	662502	0	37*	0	59
Se	.0947	ĭ	ó	15	76		-59
Sn	. 3488	Ō	2	0	0	25 33	65
Sr	.0350	1	19	18*	31*	5	30 55 11 86 59 59 65 27 41
V	.0396	0	7	0	52*		41
Y Yb	.0330 .0986	0	9 <b>*</b> 8*	0	42* 38*	0	47 5h
Zn	.0083	1	31*	12	32*	19*	7 4
Zr	.0359	2	1	0	28	2	49 54 5 66
<del></del>							<u> </u>

Only 10 elements (A1, K, Si, Na, Ti, F, Li, Ni, Zn and total C) have significant variance components at the sample level (100-meter distance), and only 5 elements (Ca, Na, Hg, Sr, and total C) have significant variance components at the township level (3-19 km). More than one-third of the elements listed in table 15 (14 of 37) have significant variability between supertownships (<19 km). These 14 elements include Ca, Fe, Mg, Si, Ti, B, Be, Cr, Cu, Ga, Li, Y, Yb, and Zn. Although soil development and characteristic vegetation on ridge tops visibly differ from that in bottom valleys, we were surprised to find that there were no significant elemental differences between soil samples collected on ridge tops and those collected in valley bottoms. This means that the ridge top and valley bottom samples can be viewed as part of the same population, and they have been considered as such in all subsequent statistical analyses.

The significant variance at the supertownship level for 14 elements indicates that these elements have a regional component of variability in the Piceance Creek Basin, and that a proper baseline for these elements must take this component into account either as a listing of supertownship means or as a map based on such means. To explore the usefulness of such means, if based on the data in hand, the variance ratio, v, may be used as a starting point. For this study, v is defined (Miesch, 1976) as the ratio of the variance among map units (supertownships here) to the sum of the variances at all levels within a map unit:

$$v = \frac{N_{v}}{D_{v}} = \frac{S^{2}}{S_{B}^{2} + S_{\gamma}^{2} + S_{\delta}^{2} + S_{\eta}^{2}}$$

where  $S^2$ ,  $S^2_{\beta}$ ,  $S^2_{\gamma}$ ,  $S^2_{\delta}$ , and  $S^2_{\gamma}$  are the logarithmic variances at the supertownship, township, section, sample, and analytical levels, respectively. Once v has been calculated for each element, it is possible to determine the number of random samples which must be collected within a supertownship to insure that two supertownships can be distinguished, at a given level of confidence, based on mean values for that element. This effective number of samples has been defined as  $n_r$  by Miesch (1976), and he presents curves at the 80- and 95-percent confidence levels for determining n\_ knowing the value of v. The n values listed in table 16 indicate that from as few as three to more than 30 random samples would have to be collected at random from within each supertownship, depending upon the element of interest, to distinguish between supertownship means, at the 80-percent confidence level. For example, it would require a mean based on iron analyses of only four random samples from each supertownship to distinguish between supertownships based on iron concentrations in soils, but it would require a mean based on ten random samples from each supertownship to distinguish confident supertownships on the basis of vanadium concentrations in soils.

Table 16 .- - Geochemical summary of surface soil in the Piceance Creek Basin, Colorado.

Data expressed in parts per million except where noted as percent (?); N, total number of samples of 140 in which element concentration was quantitatively determined; v, variance ratio of Miesch (see text);  $\mathbf{n_r}$ , minimum number of randomly selected soil samples with each supertownship required to distinguish among townships;  $\mathbf{E_r}$ , maximum acceptable value of the error variance of supertownship means;  $\mathbf{E_g}$ , observed error variance of the supertownship means based on the data in hand; n.d., not determined,  $\mathbf{n_r}$  is indefinitely large.

Element	Obscrved range	Geometric mean	Geometric deviation	N	v	n <sub>r</sub>	e <sub>r</sub>	E <sub>s</sub>
A1, Z	3.4-7.8	5.5	1.17	140	0.30	5	0.0007	0.0010
Ca, %	.46-9.8	1.9*	2.48	140	.40	4	.0285	.0408
Fe, %	1.1-2.9	1.8*	1.22	140	.38	4	.0015	.0014
Mg, 7	.51-2.7	1.0*	1.49	140	.39	4	.0053	.0065
K, %	.77-3.2	2.3	1.22	140	.07	12	.0006	.0022
Si, 7	15-34	26*	1.15	140	.24	4	.0007	.0008
Na, %	.18-3.5	1.4	1.65	140	.05	15	.0030	.0182
Ti, %	.1538	.28*	1.21	140	.40	4	.0011	.0013
C(total), %-	.87-12	3.0	. 1.69	140	. 16	6	.0076	.0144
As	<2.0-21	6.4	2.01	139	<.01	n.đ.	n.d.	n.d.
B	25-102	61*	1.35	140	.23	5	.0028	.0039
Ba	600-13,000	1,400	1.50	140	<.01	n.d.	n.d.	n.d.
Be	.88-4.4	2.4	1.46	140	.32	4	.0050	.0046
Co	1.2-16	7.9	1.77	140	. 12	7	.0089	.0114
Cr	12-110	60*	1.63	140	.20	5	.0075	.0084
Cu	<8.7-122	29*	1.94	139	.39	4	.0148	.0109
F	<400-1,600	490	1.52	112	.08	11	.0027	.0055
Ga	<2.2-39	18*	1.82	139	.11	7	.0087	.0162
Ge	<.14-2.5	.87	2.37	136	<.01	n.d.	n.d.	n.d.
Hg	.0122	.041	2.56	140	.11	7	.0205	.0529
Li	16-140	34*	1.55	140	.31	4	.0088	.0080
Mn	82-1,200	490	1.65	140	<.01	n.đ.	n.d.	n.d.
Мо	<1.04-14	5.3	2.05	134	. 12	7	.0124	.0214
Nb	<2.2-21	6.9	2.11	127	.01	n.đ.	n.đ.	n.d.
Ni	<3.4-42	21	1.83	139	.11	7	.0089	.0129
Pb	<3.3-56	26	2.09	139	. 07	12	.0080	.0208
Rb	40-190	105	1.29	140	.06	14	.0008	.0036
Sb	<.14-4.5	.90	2.70	134	.02	35	.0007	.0243
Sc	<2.1-13	6.7	1.66	131	.05	15	.0031	.0098
Se	<.11-1.2	.28	2.02	126	<.01	n.d.	n.đ.	n.d.
Sn	<.11-11	.80	3.90	121	.03	30	.0097	.0507
Sr	61-660	280	1.55	140	. 23	5	.0056	.0085
V	7.5-120	56	1.58	140	.08	10	.0037	.0090
γ	4.9-36	15*	1.52	140	. 10	8	.0038	.0068
Yb	<.28-6.2	2.1*	2.06	138	.09	10	.0091	. 0194
Zn	45-140	80*	1,23	140	.46	3	.0019	.0018
2r	54-700	270	1.55	149	.01	n.d.	n.đ.	n.đ.

Once values of  $n_r$  have been determined, it is possible to calculate the maximum acceptable error variance (E<sub>r</sub>) of the means of the mapping units (supertownships) according to the following equation (Miesch, 1976):

$$E_{r} = \frac{S_{\beta}^{2} + S_{\gamma}^{2} + S_{\delta}^{2} + S_{\gamma}^{2}}{n_{r}} .$$

Because n was determined at the 80-percent confidence level, the values of E listed in table 16 are also at the 80-percent level. E estimates the maximum permissible error variance in any computation of supertownship means. If the actual variance of the mean for a supertownship, E, based on the samples currently in hand is less than or equal to E (i.e.  $E \leq E$ ), the samples currently in hand may be used to compute suitably stable estimates of the mean concentrations in each supertownship. If E > E, additional sampling is in order before suitably stable estimates can be computed. For a balanced, hierarchical design, the observed error variance, E, is computed according to the following equation (Miesch, 1976):

$$E_{S} = \frac{S_{\beta}^{2}}{n_{\beta}} + \frac{S_{\gamma}^{2}}{n_{\beta}n_{\gamma}} + \frac{S_{\delta}^{2}}{n_{\beta}n_{\gamma}n_{\delta}} + \frac{S_{\eta}^{2}}{n_{\beta}n_{\gamma}n_{\delta}n_{\eta}},$$

where  $n_{\rm p}$ ,  $n_{\rm y}$ ,  $n_{\rm s}$ , and  $n_{\rm s}$  are the number of selected townships within supertownships, the number of sections within townships, the number of samples within sections, and the number of analyses within samples. Because the actual design was unbalanced, the effective n-values at each level are somewhat less than in a completely balanced design. The effective n-values were calculated according to techniques described by Leone, et al. (1968). For this particular design,  $E_{\rm s}$  was calculated according to the equation

$$E_{s} = \frac{S_{\beta}^{2}}{1.89} + \frac{S_{\gamma}^{2}}{2.97} + \frac{S_{\delta}^{2}}{5.39} + \frac{S_{\eta}^{2}}{7.71} .$$

E values for each of the 37 elements are listed in table 16. The condition  $E \le E$  is satisfied for five elements—Fe, Be, Cu, Li, and Zn—and maps of these five elements are shown in figures 33-35.

All five distributions show higher concentrations in the southern part of the basin and three--Cu, Li and Zn--exhibit well-defined trends in that direction. Concentrations of soil zinc increase from 68 ppm in the northeastern part of the basin to almost 100 ppm in the southwestern part. Concentrations of Li increase from 25 to 57 ppm in the same direction, and Cu concentrations increase from 18 to 50 ppm. The reason for these strong patterns is not yet clear. The geochemical trends parallel in a rough way those of the regional topography and possibly they are reflecting some altitude-related feature of the landscape.

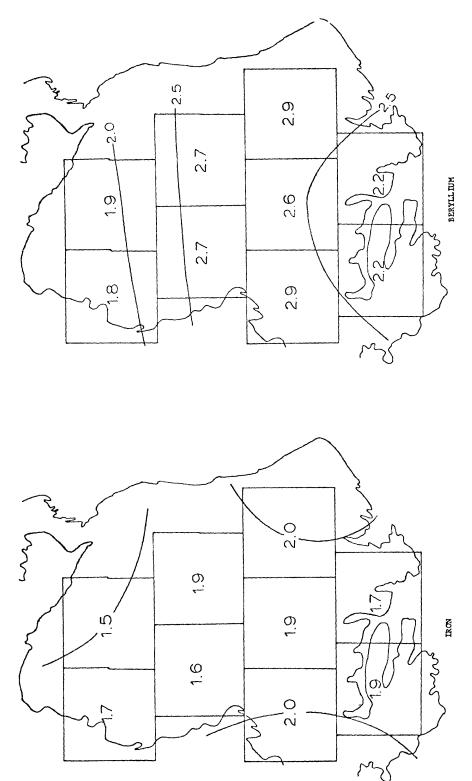


Figure 33.--Regional distribution of iron (percent) and beryllium (ppm) in surface soils in the Piceance Creek Basin, Colorado. Values are supertownship means.

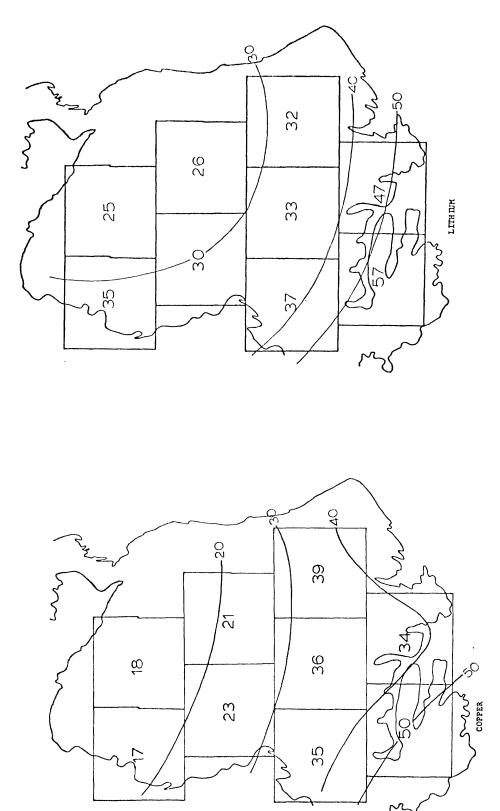


Figure 34.--Regional distribution of copper (ppm) and lithium (ppm) in surface soils in the Piceance Creek Basin, Colorado. Values are supertownship means.

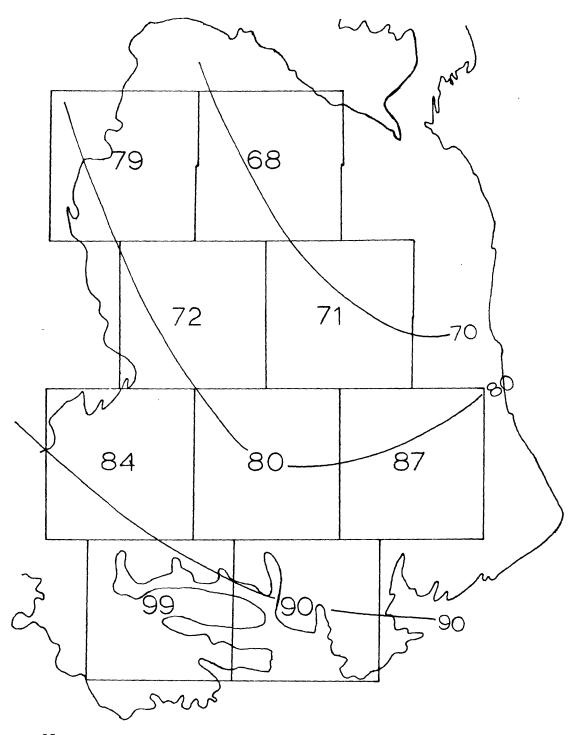


Figure 35.--Regional distribution of zinc (ppm) in surface soils in the Piceance Creek Basin, Colorado. Values are supertownship means.

A comparison of trace element concentrations in soils from the Piceance Creek Basin (table 16) with concentrations in oil shale (table 8) suggests that oil shale tends to contain substantially higher concentrations of As, Hg, and Se, and slightly higher concentrations of F, Li, and Mo. Barium and zirconium, on the other hand, tend to be substantially higher in soils than oil shale. Environmental concerns generally focus more on trace element increases in the landscape rather than decreases as a consequence of surface disruption during mining operations. Our data suggest that any land reclamation in the Piceance Creek Basin using spent shale or overburden, could induce an increase in several of the better known "noxious" trace elements.

SOIL AND GRASS CHEMISTRY NEAR THE FOUR CORNERS POWERPLANT by Jon J. Connor, Barbara M. Anderson, John R. Keith, and Josephine G. Boerngen

As part of a continuing study of the potential geochemical effects of coal-based electric power generation on the local landscape, samples of soil and grass were collected southeastward (generally downwind) from the Four Corners Powerplant in New Mexico (fig. 36). The sample design is essentially that used in sampling near the Dave Johnston and Jim Bridger Powerplants in Wyoming (Connor, Keith, and Anderson, 1976; this paper, figs. 3 and 7). The mode is:

$$Log X_{ij} = a + b (Log D) + R_i + e_{ij}$$
,

where  $X_{i,j}$  is the concentration of an element as measured by the analyst in a sample of soil or grass taken at the ith sampling locality along the traverse, a is the logarithmic concentration estimated at a distance of 1 km, b is the slope of the concentration trend, D is the distance of the locality from the powerplant in kilometers, R, is the difference between the sample and the true average for the ith locality, and e is the difference between the analyst's measurement and the true value for the sample.

In all, 14 samples of Indian rice grass (Oryzopsis hymenoides) and 28 samples of soil were collected. A sample of grass consisted of the above-ground parts of enough grass to loosely fill two quart-size refrigerator boxes. Insofar as possible, a single sample was confined to an area about 10 m on a side. In the laboratory, the plant tissue was ashed and analyzed for a variety of elements using a variety of analytical procedures (this report, fig. 42). Fluorine, sulfur, arsenic, antimony, mercury, and selenium were analyzed on the dry plant material. Two grass samples were collected up to 300 m apart in each of the seven localities; each sample was split and analyzed twice. The 28 splits were analyzed in a randomized sequence to circumvent any effects of analytical drift.

A sample of surface soil (0-2.5 cm depth) and a sample of subsurface soil (15-20 cm depth) were taken at each place a grass sample was taken. Thus, four soil samples were collected from each of the seven sampling localities. A sample of soil consisted of about 200 gms of material excluding plant debris. Each soil sample was dried at 45°C for one week, pulverized in a ceramic mill, sieved to obtain the <2 mm fraction, and split into two parts. The 56 splits were placed in a randomized sequence and analyzed according to the flow chart in figure 42, except that the emission spectrographic technique used was one based on visual rather than computer reading of the resulting photographic plate (cf. Miesch, 1976, p. 14).

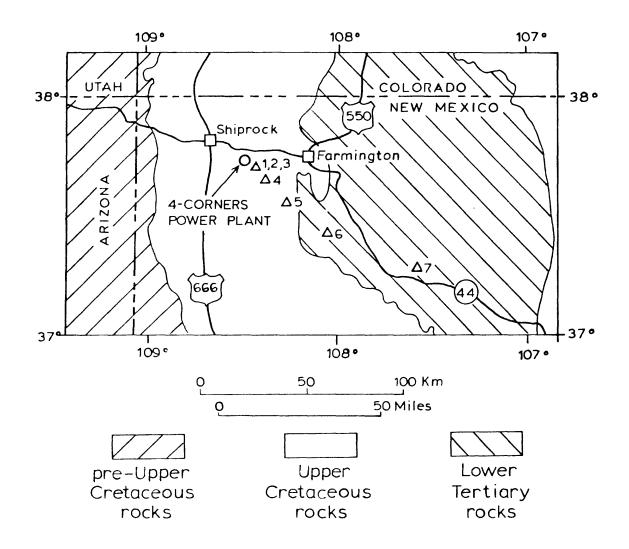


Figure 36.--Sampling localities of soil and grass southeast of the Four Corners Powerplant, New Mexico.

The analysts were J. Baker, W. Cary, A. Drenick, A. England, J. Gardner, P. Guest, J. Hamilton, T. Harms, C. Huffman, Jr., R. Havens, L. Lee, V. Merritt, H. Millard, Jr., H. Neiman, C. Papp, J. Thomas, R. Van Loenen, J. Wahlberg and T. Yager,

Results of the search for distance-related geochemical variability are summarized in table 17. Nearly half of the elements measured in grass or its ash (and the ash itself) exhibit statistically significant variation associated with distance. All trends, except silicon, decrease away from the powerplant, as would be expected if chemical pollution is occurring. Fewer trends are seen in the substrate (eight in surface soils and five in the subsurface), and about half exhibit distance-related increases rather than decreases.

A distance-related element increase is unlikely to reflect simple contamination (although it could conceivably reflect a more complicated response to chemical pollution) and, at least in the substrate, such an increase almost certainly reflects a natural variability in the soil parent. The highest concentrations for  $K_2O$  and Rb in both soil horizons were measured in samples from the two most distant localities (Appendix V, table 4). Both localities are underlain by sandy rocks of Tertiary age which, when compared to the shaly bedrock at the nearer localities, would be expected to show higher  $K_2O$  and Rb, presumably because of a higher K-feldspar content. Conversely, decreases with distance in soil CaO, MgO, and C largely reflect higher concentrations in the first three localities (Appendix V, table 4), which are underlain by carbonaceous and locally calcareous shale.

The tendency for these soil trends to involve the same major elements in both horizons ( $K_2O$ , CaO, MgO, C) further suggests a parent mineralogical control. In addition, the minor elements Rb and Ca involve both horizons and likewise probably reflect a parent control. Mn and Ca in the surface also show trends but because they increase, rather than decrease with distance, they cannot be viewed as pollutants from the Four Corners Powerplant. Thus, soil chemistry in this area shows no obvious geochemical features that could be attributed to the presence of the powerplant.

Vegetation chemistry, however, points to a large number of suspect elements (figs. 37-40), including, again, a number of major elements—Ca, K, Mg, and Si. Silicon increases with distance and may reflect a change in soil-dust composition. (The grass was not cleaned prior to analysis.) Ca, Mg, and K all decrease with distance from the powerplant but as all major constituents of living tissue (and, hence, presumably subject to biological mechanisms controlling concentration), these trends are hard to interpret, and none are particularly well developed. The trend in Ca, for example, is largely due to low concentrations in the farthest locality (fig. 38). Conceivably, the trends in Ca and Mg, which parallel similar trends in soil Ca and soil MgO, might be due to soil contamination but K cannot be so explained. The trends in Na and

Table 17 .-- Regression analysis of elements in soil and grass or its ash southeastward of the Four Corners Powerplant,

New Mexico

[\*, indicates that slope of metal trend away from power plant is significantly different at the 0.05 probability level; percentages in parentheses indicate a metal trend which increases away from powerplant; leaders (--) indicate no data)

		Grass		Soil	, 0-2.5 cm dep	rth	Soil	l, 15-20 cm de	oth
		As percent	of the total		As percent	of the total		As percent	of the total
Element or ash	Total log variance 10	Regression	Analytical	Total log variance 10	Regression	Analytical	Total log <sub>10</sub> variance	Regression	Analytical
Aluminum	0.0343	8.0	13.8	0.0044	5.1	19.2	0.0031	0.2	27.5
Ant imony	0.07821/	(4.7)	29.5	******		*******	*******	******	******
Arsanic	.0707 <u>1</u> /	(3.5)	\$2.9	*****	******	******	******		
Ash	.0126	24.9*	6.7			*****	******	*****	******
Boron	.0149	47.4*	29.7	.0093	10.42/	65.6	.0093	5.5	65.6
Barium	.0156	6.2	11.0	.0063	(4.4)	93.2	.0053	(5.1)	94.9
Cadmium	.0843	(1.3)	90.1	******		******			******
Calcium	.0059	22,5*	28.3	.0448	56.9*	0.6	.0298	57.5*	0.9
Carbon			********	.1140	30.7*	28.2	.1181	11.12/	27.3
Chromium	.0245	(<0.1)	100.0	.0223	< 0.1	58,6	.0146	5.4	89.9
Cobalt	.0272	33.6*	75,3	.0158	0.2	45.6	.0141	(0.6)	51.2
Copper	.0065	<0.1	100.0	.0249	0.5	50.2	.0234	6.5	53.4
Fluorine	.04741/	82.2*	4.5						
Gallium	.0290	18.6*	25.3	.0033	(3.5)	96.5	.0042	(0.2)	78.9
Iron	.0122	5.9	38.4	.0083	2.1	65.3	.0051	0.2	99.8
Lead	.0259	(3.6)	37.8	.0054	(21.7*)	78,3	.0078	(5.9)	56.7
Lithium	.0124	65.4*	26.1	.0057	7.2	5,4	.0040	7.0	7.6
Magnesium	.0158	21.8*	35.1	.0485	47.8*	1.1	.0244	56.1*	2.3
Manganese	.0123	(1.3)	18.6	.0082	(24.4*)	34.0	.0132	(9.3)	21.0
Hercury	.0170 <sup>1</sup> /	4.1	42.4	.0224	(0.1)	62.1	.0293	(0.3)	47.6
Molybdeeum	.0567	56.8*	43.1			******	******	******	
Nickel	.0385	36.2*	57.1	.0279	2.1	44.7	.0222	(1.3)	56.3
Phosphorus	.0132	(0.8)	37.8	******		*******			******
Potassium	.0214	16.6*	17.1	.0020	(54.3*)	1.6	<b>.0</b> 015	(41.2*)	2.1
Rubidium		*******		.0028	(29.0*)	12,4	.0019	(15.1*)	18.5
Scandium				.0530	(2.1)	60.4	.0526	4.3	60.8
Selenium	.05341/	60.8*	7.8		******		******	******	******
Silicon	.0041	(38.5*)	17.5	.0004	(8.5)	34.6	.0003	(1.1)	47.9
Sodium	.0358	45.1*	11.0	.0032	9.3	2.0	.0032	8.3	2.0
Strontium	.0352	46.3*	12.7	.0190	4.5	23.3	.0137	(2.8)	32.5
Sulfur	.0413 <sup>1</sup> /	46.2*	7.6					******	
Thorium		*****		.0060	(2.7)	30.7	.0064	(8.6)	28.8
Titanium	.0268	<0.1	38.7	.0106	(1.9)	5.9	.0072	(2.8)	8.6
Uraniom	.0405	3.9	42.5	.0056	1.7	8.1	.0051	0.4	8,9
Vanadium	.0251	4.4	39,8	.0183	3.8	59.8	.0114	9.1	90.9
Ytterbium			******	.0056	(0,3)	33.8	.0227	1.7	9.7
Yttrium			*********	.0060	(2.3)	55.0	.0093	(0.1)	34.0
Zinc	.0087	2.7	17.3	.0035	24.2*	2.5	.0061	21.6*	3.5
Zirconium	.0630	0.5	99.5	.05/+4	(3.6)	26.4	.0530	1.1	98.9

and S (figs. 37 and 39) are fairly strong, although their interpretation is fraught with the same problems as K, Ca, and Mg since they are also essential elements in plant tissue. Ash weight of grass also decreases away from the powerplant, in a fashion clearly related to the variation in K (r=0.56 for Log Ash vs. Log K in 14 samples, significant at the 0.05 probability level). Log Ash is not significantly correlated with Log Ca (r=-0.18), Log Mg (r=-0.35), or Log Si (r=0.39), indicating that soil contamination is probably not an important contributor to plant ash. The underlying cause for these seven trends remains unknown but does not appear to involve, in an important way, simple element contamination from either nature (soil dust) or man (powerplant). Of the remaining 9 suspect elements, the strongest trends in vegetation are in F and Se (fig. 37), both volatile elements and both suspected pollutants at the Dave Johnston Powerplant in Wyoming (Connor, Keith, and Anderson, 1976; this report, fig. 4). Trends for Co, and Sr (figs. 39 and 40) are fairly strong, and these three must be considered as suspect pollutants. Both have been implicated at the Dave Johnston Powerplant (Connor, Keith, and Anderson, 1976; this report, fig. 4). The trends in Mo, Ni, Ga, Li, and B (figs. 39 and 40) largely reflect concentrations in the outer three or outer four localities, which suggests a possible substrate control on concentration.

Thus, geochemical work with three vegetation types (sagebrush, lichen, and grass) and two soil horizons (surface and subsurface) around three powerplants in the Western Coal Regions has demonstrated the complexity of attempts to quantify potential element emissions by use of "natural" monitors (cf. Connor, Keith, and Anderson, 1976; U.S. Geological Survey, 1974b, p. 14-29; U.S. Geological Survey, 1975, p. 50-57; this report, figs. 4, 8-10). Based on examination of distance-related geochemical variability, a large number of elements have been implicated as suspect pollutants. Most soil elements so implicated appear to be better interpreted as reflecting natural geochemical changes in the soil substrate (that is, geologic control), but this explanation seems less satisfactory for the interpretation of distance-related plant chemistry.

The most likely suspect elements at this time are Se, F, and Sr because all exhibit significant distance-related decreases in vegetation near the operating powerplants. In addition, Se and F are "volatile" elements and might be expected in flue gasses. Contradictorily, Se and F show a similar distance-related variation in vegetation near the Jim Bridger Powerplant before this powerplant was fully operational. Their trends are not as well developed here as at Dave Johnston and Four Corners (figs. 8 and 9). These mixed results demonstrate that vegetation has greater promise than soil as an element monitor but that considerably more work is required before such monitors can be used with much confidence.

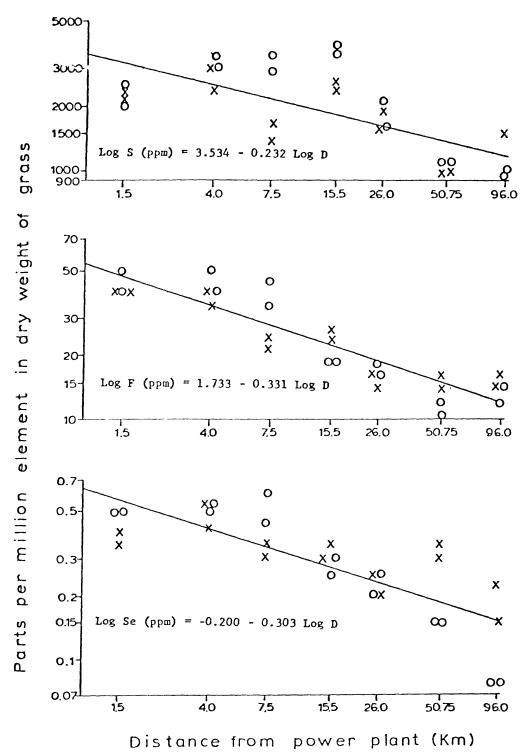
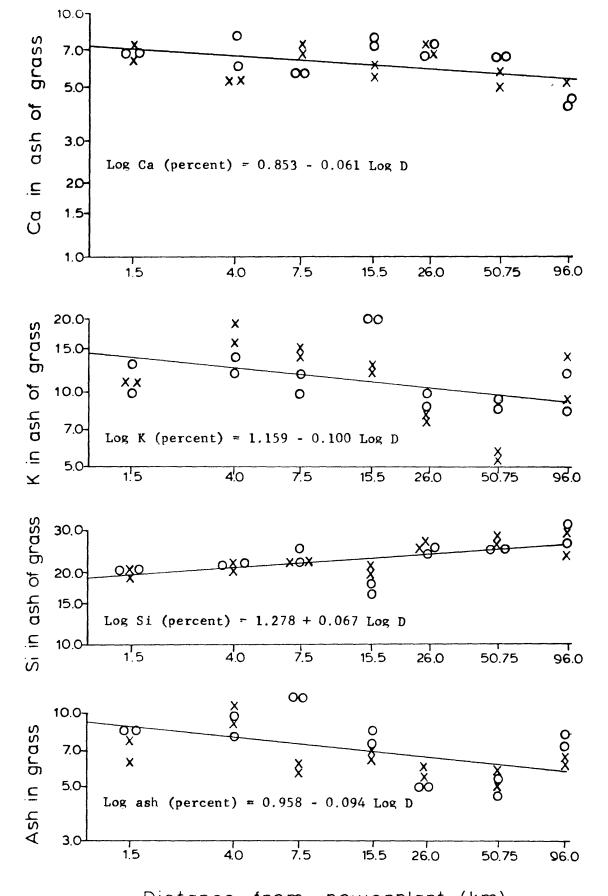


Figure 37.--Parts per million of selenium, fluorine, and sulfur in dry weight of grass as a function of distance (D) from the Four Corners Powerplant, New Mexico. Cross (x) indicates duplicate analysis of first grass sample in each sampling locality, and circle (o) denotes duplicate analysis of second grass sample in each sampling locality.



Distance from powerplant (km)

Figure 38.--Percent ash, and percent silicon, potassium, and calcium in ash, of grass as a function of distance (D) from the Four Corners Powerplant, New Mexico. Cross (x) indicates duplicate analysis of first grass sample in each sampling locality, and circle (o) denotes duplicate analysis of second grass sample in each sampling locality.

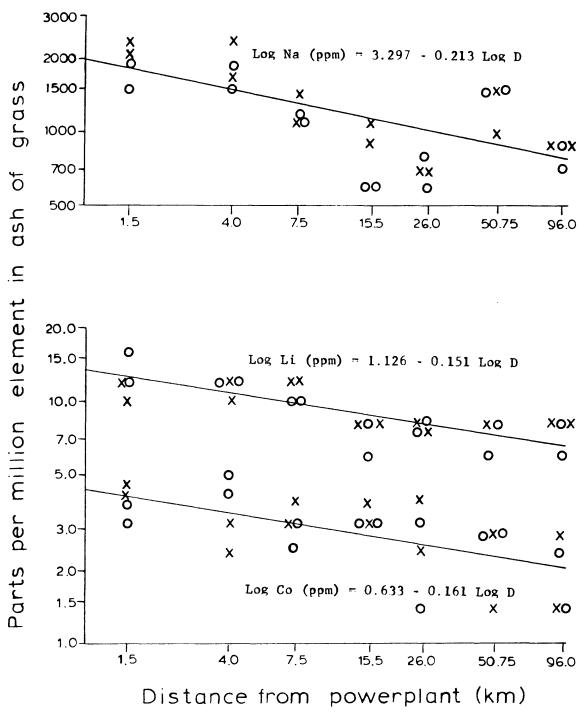
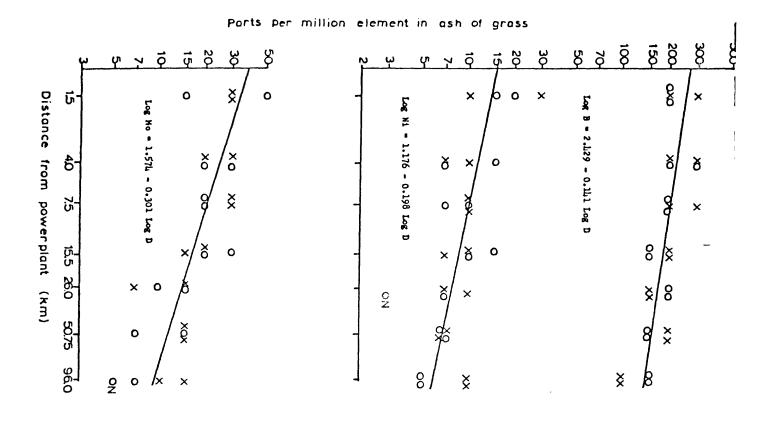


Figure 39.-- Parts per million of cobalt, lithium, and sodium in ash of grass as a function of distance (D) from the Four Corners Powerplant, New Mexico. Cross (x) indicates duplicate analysis of first grass sample in each sampling locality, and circle (o) denotes duplicate analysis of second grass sample in each sampling locality.



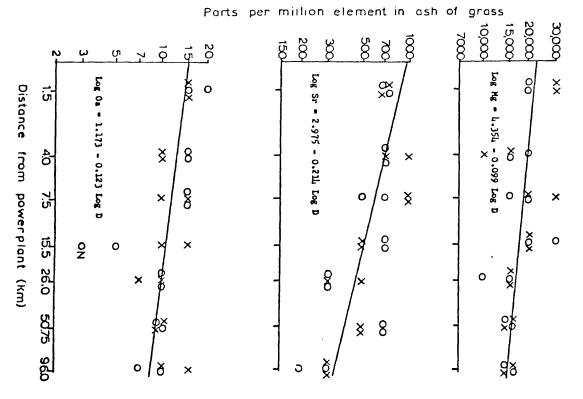


Figure 40.--Parts per million of molybdenum, nickel, boron, gallium, strontium, and magnesium in ash of grass as a function of distance (D) from the Four Corners Powerplant, New Mexico. Cross (x) indicates duplicate analysis of first grass sample in each sampling locality, and circle (o) denotes duplicate analysis of second grass sample in each sampling locality. N indicates concentration is below limit of analytical determination.

# STREAM SEDIMENT CHEMISTRY IN THE OIL-SHALE REGION by James M. McNeal, Gerald L. Feder, Charles D. Ringrose and Ronald W. Klusman

#### Introduction

The oil-shale region of western Colorado and eastern Utah may be developed to provide fossil fuel materials from the rock of the area. Four sites, two each in Utah and Colorado, have been leased to private companies for mine development. Prior to mine development, background information on surface-water quality is needed so that environmentally acceptable mining plans may be developed and the mining operations monitored. However, most of the streams which drain the least sites are dry most of the year and commonly have only slight flows for years in a row. In the short period of time allotted to collect background data on these streams, there may not be enough runoff events to obtain sufficient data. By sampling fine-grained stream sediments from the beds of these dry streams, it may be possible to obtain useful background information on concentrations of chemical constituents in the sediments in lieu of collecting surface waters. This data might then be used to recognize changes in the chemical composition of stream sediments possibly resulting from changes in water chemistry.

This report describes some preliminary results of two similar, but independently initiated, studies of a stream-sediment chemistry undertaken to examine problems which might arise in any attempts to use stream sediments as a natural monitoring medium. A major problem is the work (cost) required to obtain valid background information on the chemical composition of stream sediments. This, in turn, involves the determination of appropriate sampling densities. The first study was undertaken by McNeal and Feder and focuses on the geochemical variability expected among streams in the oil shale-bearing areas of Colorado and Utah. The second study was undertaken by Klusman, Ringrose, and McNeal and focuses on the degree of geochemical variability expected at various sampling intervals along stream courses in the Colorado parts of the oil-shale region (Piceance Creek Basin).

Cottonwood, Asphalt, Ryan, and Big Duck Drainages

In this study, two drainages in the Uinta Basin and two in the Piceance Creek Basin were selected for sampling (fig. 41). Each of the four stream drainages may undergo change in stream flow and sediment yield related to oil-shale mining and processing. In order to characterize each stream, eight samples were collected—three samples were collected from random sites within three intervals of equal length along the main channel of the named stream, and five additional samples were collected above alluvial fans at the mouths of five randomly selected tributaries entering the main stream.

The resulting data were examined by a nested analysis of variance design containing four levels. The top level reflects differences between the two major basins (Uinta and Piceance); the second level reflects

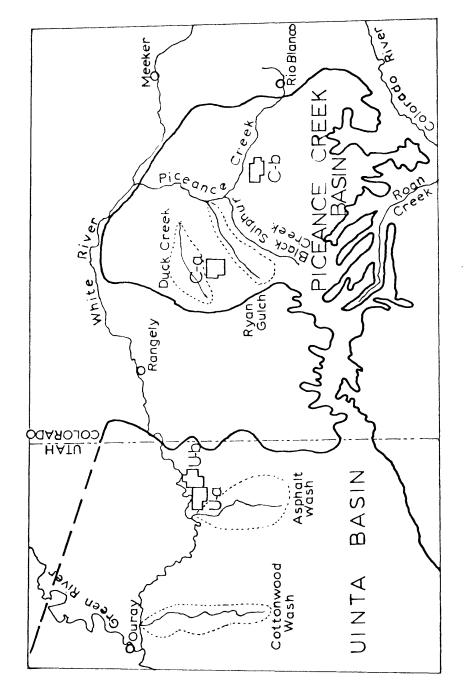


Figure 41.--Stream sediment sampling localities in the Piceance Creek and Uinta Basins, Colorado and Utah. Dashed areas indicate drainage basins that were sampled.

differences among the paired drainages within each basin; the third level reflects differences among the eight samples taken within each of the four drainages, and the lowest level reflects differences among splits of the randomly selected samples.

All samples were collected from dry stream channels in areas where fine sediments had accumulated. At each locality, approximately two kilograms of sediment were composited from material taken at seven to ten sites within 20 meters of each other and at depths of no more than three centimeters. The samples were air dried at 40°C, then sieved through a 150-micron stainless steel screen. The <150-micron sediment was then sent to the laboratory for analysis. All samples, including replicates, were coded and placed in random order prior to analysis. Spectrographic analysis was performed in the U.S. Geological Survey, Water Resources Division laboratories in Denver, Colorado under the supervision of P. R. Barnett. Wet chemical analysis was performed in the U.S. Geological Survey, Water Resources Division laboratories in Salt Lake City, Utah under the supervision of R. L. McAvoy.

The analysis of variance results shown in table 18 indicate that nearly two-thirds of the constituents exhibit significant differences between the four streams. In particular, the fact that Ca, Mg, Sr, and carbonate C each have greater than 70 percent of their total variance associated with the between-stream level implies that it is the presence or absence of carbonate minerals, presumably detritus of the calcareous Green River Formation that causes the main difference between streams. Na, K and Ba also have significant variance components at this level, indicating that the concentration of alkali-feldspar detritus may also vary significantly between streams. Possibly, some of the Na occurs in NaHCO<sub>3</sub> (nahcolite), or NaAlSi $_2$ O $_4$ ·H $_2$ O (analcime).

In view of the large number of constituents with significant variance at the between-stream level, it seems reasonable that future stream-sediment work should be concerned with examining differences among streams if an appropriate number of samples  $(n_r)$  are randomly collected from each stream to stabilize its mean;  $n_r$  can be estimated from the variance ratio, v, of Miesch (1976):

$$v = (P_B + P_S)/(P_L + P_A)$$

where  $P_B$ ,  $P_S$ ,  $P_L$  and  $P_A$  are percentages of variance (from table 18) estimated for the between-basins, between-streams, between-samples, and between-analyses levels, respectively. If interest focuses on differences among streams in one basin rather than both, the numerator becomes reduced to  $P_S$  only. From the variance ratio and figure 2 of Miesch (1976, p. 9), the minimum number of randomly selected sample composites needed from each stream can be found. In general, the number of samples required is inversely related to the size of the variance ratios. The following

Table 18.--Analysis of variance results, summary statistics, and geochemical baselines for stream sediments of the Piceanca Creek and Uinta Basins, Colorado, and Utah

[Data in parts per million, except where noted as percent (%); \*, component significantly different from zero at the 0.05 probability level; leaders (---), summary data given in table 19]

	An	alysis of lo	ogarithmic	variance			Summary	statistica	
ļ		Perce	ent of tota	l variance	:		Jupually		
Constituent	Total <sup>Log</sup> 10 variance	Between basins	Between streams	Within streams	Analy- tical error	Geometric mean	Geometric deviation	Geometric error	Expected 95: range (Baseline)
Al, %	0.0132	< 0.1	2.7	< 0.1	97.3	4.28	1.30	1,30	
As	.0906	3.8	< .1	92.1*	4.1	6.5	2.00	1.15	1.7-25
В	.0200	< .1	48.1*	2.6	49.3			1.26	
Ва	.0132	< .1	55.2*	31.4	13.4			1.10	
Ве	.0346	< .1	< .1	71.0	29.0	3.3	1.53	1.26	1.6-6.7
C, carbonate, %	.2509	< .1	86,1*	1.7	12.2		<u> </u>	1.50	
C, organic, %	.1634	35,5	38,4*	21.7*	4.3			1.21	
Ca, %	.0626	< .1	79.6*	20.2*	.2			1.03	
Co	.0146	< .1	35.3*	46.4	18.3			1,13	
Cr	.0968	< .1	< .1	40.1	59.9	61	2.05	1.74	25-150
Cu	.0159	5.4	< .1	82.3*	12.3	21	1.34	1.11	12-36
·	.2264	< .1	2.6	53.0	44.4	7.8	2.99	2.08	1.5-40
e, %	.0269	< .1	31'.3*	54.3	14.4			1.15	
Ga	.0150	< .1	36.0*	25.2	38.8		•	1.19	
к, 2	.0074	< .1	67.8*	< .1	32.2			1.12	
La	.0536	10.7	< .1	79.4*	10.0	45	1.70	1.18	16-124
L1	.0260	< .1	54.0*	39.54	6.5			1.10	
4g, %	.0387	< .1	71.9*	< .1	28.1			1.27	
in	.0081	< .1	44.5*	34.4	21.2			1.10	
Na, %	.0137	< .1	26.1*	67.9~	6.0			1.07	
ур	.0162	< .1	52.2*	< .1	47.8			1.22	
N1	.0860	< .1	< .1	48.1	51.9	48	1.76	1.63	19-120
P, %	.0045	4.0	3.0	84.9*	8.0	.082	1.17	1.04	.0611
Pb	.9237	6.0	29.7*	< .1	64.3			1.33	
Sc	.0225	< .1	30.0*	27.1	43.9			1.26	
S <b>r</b> -	.0383	< .1	71.0*	27.4*	1.7			1.06	***
ri, %	.0300	< .1	5 <b>.3</b>	50.4	44.3	.030	1.49	1.30	.020050
v	.0208	< .1	52.7	< .1	47.3			1.25	
(	.0146	10.6	23.6*	23,6	42,1			1.20	
(b	.0210	< .1	24.6×	47,6	27.7			1.19	
Zn	.1066	< .1	< .1	63.7	36.3	245	·2.12	1.57	74-B15
Zr	.0379	26.3	11.4	46.9	15.4	215	1.57	1.19	94-490

table lists the minimum number of samples  $(n_r)$  to be randomly collected from a stream and the constituents that can be described for each of two confidence levels:

n <sub>r</sub>	Constituents	
	80 percent confidence level	95 percent confidence level
3	B, Ba, CO <sub>3</sub> , C <sub>org</sub> , Ca, Co, Fe, Ga, K, Li, Mg, Mn, Nb, Pb, Sr, V	CO <sub>3</sub> , Ca, Mg, Sr
4	The above, plus Na, Sc, Y, Yb	The above, plus C <sub>org</sub> , K
5	The above	The above, plus B, Ba, Li, Nb, V
6	The above, plus Zr	The above, plus Mn
7	The above	The above, plus Co, Ga
8	The above	The above, plus Fe, Pb
9	The above	The above, plus Sc
10	The above	The above, plus Na, Y
11	The above	The above, plus Yb

Obviously, there is a trade-off between the number of composites collected from a stream in an area and the number of constituents that can be adequately described in terms of stream averages. If 20 constituents are to be so described at the lower level of confidence, then only five composites need to be randomly collected along the course of each stream in the study area. At the higher level of confidence (95 percent), the collection of five composites will result in adequate descriptions for only 11 constituents. Ten composites per stream would permit the mapping of 19 constituents at this higher level of confidence. The collection of one additional composite would provide information on Yb, but the lack of interest in Yb suggests that the extra composite is probably not worth the additional 10 percent increase in sampling effort. The use of ten composites rather than eight may be justified because of the desirability of obtaining reliable data on Na. A number of elements, including the interesting and potentially environmentally important A1, As, Be, Cr, Cu, F, Ni, P, Ti, and Zn, exhibit little variation between streams or basins, so additional sampling is probably not needed for these elements to provide provisional regional baselines for the area of study as a whole (table 18).

The remaining elements are too variable among streams to permit regional baseline estimation, so valid baseline estimation must be undertaken on a stream-by-stream basis. In order to distinguish among streams at the 80 percent confidence level, each stream average must be based on at least four randomly selected composites. Because the eight composites actually collected from each stream drainage are not nested (although they are stratified), it is likely that they may be viewed as fulfilling these sampling requirements. Based on such data, provisional summary estimates are listed in table 19 for the 20 constituents so affected.

#### Roan and Black Sulfur Creeks

This study is aimed largely at quantifying the major scales of geochemical variability along two selected streams in the Piceance Creek Basin. The sampling design is a six-level, nested analysis of variance design.

The six levels used in this design define components of geochemical variability (1) between streams, (2) between 10-km intervals, (3) between 1-km intervals, (4) between 200-m intervals, (5) between 20-m intervals, and (6) analytical error. The two streams chosen at the top level are Roan Creek, which flows nearly east-west in the southern part of the basin, and Black Sulfur Creek, which flows nearly north-south in the central portion of the basin (fig. 41). The Roan Creek drainage crosses exposures of the lower Uinta Formation, all of the Green River Formation, and the upper Wasatch Formation. Black Sulfur Creek lies mostly in the upper Green River and lower Uinta Formations. Two major sample locations were picked on each stream and separated by 10 km. The design is geographically balanced and in each locality, two segments of stream 200 m in length were randomly located about 1 km apart. In each 200-m length, two segments about 20-m long were randomly located, and in each 20-m segment, two sampling sites were randomly located. Ten samples of the 32 collected were randomly selected for duplicate analysis, and all 42 were placed in a random order prior to chemical analysis.

The samples were collected by hand and placed in cloth bags and allowed to air-dry. They were then disaggregated with a mortar and pestle and passed through a 80-mesh sieve. The -80 mesh fraction was retained for analysis. All samples were collected away from the influence of stream banks and were not composited. They were analyzed by John C. Hamilton who used the semiquantitative emission spectrographic technique described in Miesch (1976, p. 14).

The analysis of variance results in table 20 show that little variation occurs between the two streams and that most of the variation is associated with scales of 1-10 km and 0-20 m. Thus, most of the variation occurs either at very local scales or at relatively large scales. There is no significant variation occurring at the 20-200 m interval for any of the elements, and only three elements (B, Cu, and Mg) have significant variation at the 200 m - 1 km interval.

Table 19, -- Surmary statistics for Asphalt Wash and Cottonwood Wash of Uinta Basin, and Duck Gulch and Ryan Gulch

of Piceance Creek Basin

[Data in parts per million except where noted as percent (X)]

GooderInt (colored 17).         Choose (seed 37).         Choose (seed 37).			Asphalt Wash	1	0	Cottonwood Wash	sh		Duck Creek			Ryan Gulch	
	Constituent	Geometric mean	Geometric deviation	Expected 95% range (Baseline)	Geometric	Geometric deviation	Expected 95% range (Bascline)	Geometric mean	Geometric deviation	Expected 95% range (Baseline)	Geometric	Geometric deviction	Expected 95% range (Baseline)
780         11.8         560-1,090         1,080         1,28         660-1,770         935         1,14         720-1,220         725         1,28           .33         1,66         .34-2,56         .26         1,26         1,13         1,13         1,29         1,49	3	24.0	1.17	39-74	38.0	1.40	19.0-74.0	34.0	1.27	21.0-55.0	53.0	1.33	30.0-94.0
1.5         1.6         1.4-2.56         1.2         1.1-3         1.19         1.44         94-4-04         1.39         1.15         1.49         1.24         1.25         1.14         1.26         1.19         1.26         1.19         1.26         1.19         1.26         1.19         1.26         1.19         1.26         1.19         1.26         1.19         1.26         1.19         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.29         1.19         1.29         1.29         1.19         1.29         1.29         1.29         1.19         1.29         1.29         1.29         1.19         1.29         1.29         1.19         1.29         1.29         1.19         1.29         1.19         1.29         1.19         1.12	es	780	1.18	560-1,090	1,080	1,28	660-1,770	935	1.14	720-1,220	725	1.20	505-1,040
4.50         1.31         .45-1.42         .23         1.84         .07-85         1.26         1.79         .39-4.04         1.11         1.44           4.50         1.30         2.36-8.37         3.11         1.06         2.77-3.49         7.51         1.48         3.43-16.4         2.96         1.15         2.96         1.15         2.96         1.15         2.96         1.15         2.96         1.15         1.26         2.96         1.15         1.27         1.28         3.43-16.4         2.96         1.15         1.15         1.29         1.20         4.18         1.15         1.29         2.96         1.15         1.24         2.96         1.15         1.29         1.20         4.18         1.29         1.20         4.18         1.29         1.29         1.29         1.29         2.41         1.29         1.29         1.20	, co2, z	.93	1.66	.34-2.56	.26	1,43	.1353	1.95	1.44	70.4-46.	.38	1.53	.1689
	, organic,		1.33	.45-1.42	.25	1.84	.0785	1.26	1.79	.39-4.04	1:31	1.44	.63-2.72
7.0         1.20         4.9-10.1         8.4         1.40         4.3-16         5.9         1.20         4.1-8.5         8.0         1.20            1.9         1.26         1.60         1.0-6.7         1.7         1.38         1.9-2         2.4         1.24            1.7         1.19         1.2-3.0         2.6         1.60         1.0-6.7         1.7         1.38         9.8-23         2.4         1.24            2.22         1.04         2.05-2.40         1.64         1.10         1.36-1.38         2.02         1.69         1.73-2.36         1.39         1.73         1.74<	.a, 7	4.50	1.38	2,36-8,57	3.11	1.06	2.77-3.49	7.51	1.48	3,43-16,4	2.96	1.15	2,24-3,91
1.9         1.26         1.06-5.7         1.7         1.38         .9-3.2         2.4         1.24            1.7         1.17         1.2-3         2.6         1.64         1.0-6.7         1.7         1.36         1.24         1.3-31         1.24         1.3-31         1.24         1.3-31         2.2         1.34         1.32         2.2-3.4         1.64         1.10         1.36-1.36         2.02         1.08         1.73-2.36         1.98         1.17         1.3         1.3         22-65         31         1.17         1.3            36         1.32         2.0-1.93         2.3         1.18         1.7-32         38         1.31         22-65         31         1.17         1.3         1.3         1.3         1.3         1.3         1.3         1.3         1.3         1.3         1.3         1.4         1.4         1.4         1.4         1.3         1.4         1.2         1.4         1.1         1.9         1.2         1.4         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2         1.2 </td <td> 60</td> <td>7.0</td> <td>1.20</td> <td>4.9-10.1</td> <td>4.8</td> <td>1.40</td> <td>4.3-16</td> <td>5.9</td> <td>1.20</td> <td>4.1-8.5</td> <td>8.0</td> <td>1.20</td> <td>5.6-12</td>	60	7.0	1.20	4.9-10.1	4.8	1.40	4.3-16	5.9	1.20	4.1-8.5	8.0	1.20	5.6-12
17         1.17         12-23         20         1.24         13-31         15         1.24         9.8-23         2.02         1.24         1.39-1.98         1.20         1.24         1.39-2.36         1.39         1.17         1.39-2.36         1.99         1.17         1.39-2.36         1.19         1.30-1.98         2.02         1.08         1.73-2.36         1.19         1.10         1.30-1.98         2.02         1.08         1.21         1.26         1.17         1.29         1.20		1.9	1.26	1.2-3.0	2.6	1.60	1.0-6.7	1.7	1.38	.9-3.2	2.4	1.24	1.6-3.7
	a	11	1.17	12-23	20	1.24	13-31	1.5	1.24	9.8-23	22	1.34	12-40
	F. 5	2.22	1.04	2.05-2.40	1.64	1.10	1.36-1.98	2.02	1.08	1.73-2.36	1.98	1.17	1.45-2.71
1.17         1.29         .70-1.95         .65         1.19         .4692         .95         1.20         .66-1.37         .68         1.27            510         1.07         445-585         600         1.20         415-865         615         1.16         455-830         480         1.20            2.45         1.11         1.99-3.02         1.83         1.52         .79-4.23         2.49         1.09         1.20            1.3         1.22         1.65-3.65         1.4         1.21         10-20         9.2         1.30         1.49         1.15         1.49         1.49         1.19         1.19         1.20         9.2         1.30         1.49         1.14         1.13         1.14 </td <td> J.</td> <td>36</td> <td>1.32</td> <td>21-63</td> <td>23</td> <td>1.18</td> <td>17-32</td> <td>38</td> <td>1.31</td> <td>22-65</td> <td>31</td> <td>1.28</td> <td>19-51</td>	J.	36	1.32	21-63	23	1.18	17-32	38	1.31	22-65	31	1.28	19-51
510         1.07         445-585         600         1.20         415-865         615         1.16         455-830         480         1.20            2.45         1.23         1.24         1.11         1.99-3.02         1.83         1.52         779-4.23         2.49         1.09            13         1.23         8.6-20         14         1.21         10-20         9.2         1.30         5.4-16         1.4         1.15            18         1.16         13-24         19         1.26         5.7-14         13         8.6-20         19         1.11            12         1.33         6.8-21         11         1.26         5.7-14         13         8.6-20         19         1.11            12         1.33         6.8-21         11         1.28         67-18         7.4         1.34         4.1-13         1.21         1.34            295         1.30         1.25-20         1.40         61-235         73         1.11         340-570         225         1.23            29         1.13         22-38         1.24         1.27	2 '2;	1.17	1,29	.70-1.95	\$9.	1,19	7695	56.	1.20	.66-1.37	89.	1.27	.42-1.10
2.45         1.22         1.65-3.65         2.45         1.11         1.99-3.02         1.83         1.52         79-4.23         2.49         1.09            13         1.23         8.6-20         14         1.21         10-20         9.2         1.30         5.4-16         14         1.15            18         1.16         13-24         19         1.26         5.7-14         13         8.6-20         19         1.14         1.13         1.14         1.14         1.14         1.14         1.14         1.14         1.14         1.14         1.14         1.14         1.14         1.29 <t< td=""><td> uj</td><td>510</td><td>1.07</td><td>445-585</td><td>009</td><td>1.20</td><td>415-865</td><td>615</td><td>1.16</td><td>455-830</td><td>480</td><td>1.20</td><td>335-690</td></t<>	uj	510	1.07	445-585	009	1.20	415-865	615	1.16	455-830	480	1.20	335-690
13         1,23         8,6-20         14         1,21         10-20         9,2         1,30         5,4-16         14         1,15            18         1,16         13-24         19         1,26         5,7-14         13         1,23         8,6-20         19         1,14            12         1,33         6,8-21         11         1,28         67-18         7,4         1,34         4,1-13         12         1,33            295         1,30         175-500         420         1,36         225-775         440         1,14         340-570         225         1,29         1,29            91         1,18         65-130         1,20         1,40         61-235         73         1,13         57-93         1,29         1,23            29         1,15         22-38         34         1,27         21-55         22         1,30         1,30         1,44,4         3,1         1,53         1,3-7,3         2,1         1,26         1,3-3,3         2,9         1,15         2,9         1,15         2,1         2,1         1,26         1,3-3,3         2,9         1,15         2,9 </td <td>ia, %</td> <td>2.45</td> <td>1.22</td> <td>1.65-3.65</td> <td>2,45</td> <td>1.11</td> <td>1.99-3.02</td> <td>1.83</td> <td>1.52</td> <td>.79-4.23</td> <td>2.49</td> <td>1.09</td> <td>2.10-2.96</td>	ia, %	2.45	1.22	1.65-3.65	2,45	1.11	1.99-3.02	1.83	1.52	.79-4.23	2.49	1.09	2.10-2.96
1.16         13-24         19         1.26         5.7-14         13         1.23         8.6-20         19         1.14            12         1.33         6.8-21         11         1.28         67-18         7.4         1.34         4.1-13         12         1.33            295         1.30         175-500         420         1.36         225-775         440         1.14         340-570         225         1.29         1            91         1.18         65-130         120         1.40         61-235         73         1.13         57-93         120         1.23            29         1.15         22-38         34         1.27         21-55         22         1.30         13-37         27         1.21            2.5         1.32         1.4-4.4         3.1         1.53         1.3-7.3         2.1         1.26         1.3-3.3         2.9         1.15         2	q1	13	1.23	8.6-20	14	1,21	10-20	9.2	1.30	5.4-16	14	1.15	11-19
12 1.33 6.8-21 11 1.28 67-18 7.4 1.34 4.1-13 12 1.33 6.8-21 1.30 1.5-500 420 1.36 225-775 440 1.14 340-570 225 1.29 1.29 1.20 1.40 61-235 73 1.13 57-93 120 1.23 1.23 1.23 1.23 1.23 1.23 1.23 1.23	q	18	1.16	13-24	19	1.26	5.7-14	ដ	1.23	8.6-20	19	1.14	15-25
295 1.30 175-500 420 1.36 225-775 440 1.14 340-570 225 1.29 1 91 1.18 65-130 120 1.40 61-235 73 1.13 57-93 120 1.23 29 1.15 22-38 34 1.27 21-55 22 1.30 13-37 27 1.21 2.5 1.32 1.4-4.4 3.1 1.53 1.3-7.3 2.1 1.26 1.3-3.3 2.9 1.15 2		12	1,33	6.8-21	ı	1.28	67-18	7.4	1.34	4.1-13	12	1.33	6.8-21
91 1.18 65-130 120 1.40 61-235 73 1.13 57-93 120 1.23 1.23	as	295	1.30	175-500	420	1.36	225-775	077	1.14	340-570	225	1.29	135-375
29     1.15     22-38     34     1.27     21-55     22     1.30     13-37     27     1.21        2.5     1.32     1.4-4.4     3.1     1.53     1.3-7.3     2.1     1.26     1.3-3.3     2.9     1.15		16	1.18	65-130	120	1.40	61-235	73	1.13	57-93	120	1.23	79-180
2.5 1.32 1.4-4.4 3.1 1.53 1.3-7.3 2.1 1.26 1.3-3.3 2.9 1.15		29	1.15	22-38	34	1.27	21-55	22	1.30	13-37	27	1.21	18-40
		2.5	1.32	1,4-4,4	3.1	1.53	1.3-7.3	2.1	1.26	1.3-3.3	2.9	1,15	2,2-3,8

Table 20.--Geochemical summaries for stream sediments of Roan and Black Sulfur Creeks, Colorado.

[Data given in parts per million, except where noted as percent (%); an asteriak (\*)

indicates variance component is significantly different from zero at the 0.05

probability level; leaders (---), data insufficient for estimation]

			Analysis o	f logarithmic	variance			<u> </u>	S	tatistics	······································
			Pe	rcent of total	variance				Summary s	STACISTICS	
Element	Total Log <sub>10</sub> variance	Between streams	1-10 km	200 m-1 km	20-200 m	0-20 m	Analy- tical error	Geometric mean 1/	Geometric deviation 1/	Geometric error	Expected 95: Range (Baseline) 1
A1, %	0.0223	25*	3	6	< 1	33	33	6,0, 7.6	1.32, 1.20	1.22	4.1-8.8,
В	.0201	< 1	< 1	38*	< 1	15	47	44	1.39	1.25	27-71
Ba	.0168	6	< 1	13	4	23	54	940	1.35	1.25	630-1,400
Ca, %	.0253	< 1	68*	<1 .	7	3	22	5.4	1.44	1.19	2,8-10
Co	.0289	38	29*	< 1	< 1	17	16	8	1.48	1.17	3.9-16
Cr	.1048	58	21*	1	< 1	11	9	56	2.11	1.25	13-230
Cu	.0189	8	53*	11*	< 1	8	20	17	1.37	1.15	9.6-30
Fe, Z	.0156	< 1	58*	2	< 1	35*	5	2.2	. 1.33	1,07	1.3-3.8
G <b>a</b>	.0106	4 <b>9</b> *	8*	< 1	7	< 1	37	15, 20	1.09, 1.19	1,16	, 17-24
K, Z	.0015	< 1	< 1	3	< 1	97*	< 1	3.1	1.09	< 1.01	2.6-3.7
Mg, Z	.0081	3	13	35*	< 1	19	30	1.4	1.23	1.12	.99-2.0
Mn	.0193	27	12*	5	< 1	20	36	260	1.38	1,15	160-430
Na, Z	.0131	69*	< 1	< 1	< 1	6	25	2.2, 3.0	1.18, 1.09	1.14	1.8-2.7, +
NÍ	.0078	24*	5	14	< 1	47*	10	15, 18	1,07, 1.20	1,07	, 13-25
Pb	.0137	1	< 1	< 1	< 1	61*	38	18	1.31	1.18	12-28
Sc	.0186	17	60*	< 1	< 1	< 1	23	8	1.37	1.16	4.6-14
Sr	.0027	< 1	12	5	< 1	< 1	83	520	1.13	1,12	470-570
Ti, Z	.0450	11	25*	<b>&lt;</b> 1	< 1	38*	26	.21	1.63	1.28	.09149
v	.0188	< 1	40*	6	< 1	33*	21	70	1.37	1,16	40-120
Y	.0135	11	< 1	< 1	< 1	39	50	22	1.31	1.21	15-32
Yb	.0195	< 1	< 1	< 1	< 1	45	55	2	1.38	1.27	1.3-3.1
Zr	.0470	5	< 1	< 1	< 1	87*	8	180	1.65	1.15	69-470

<sup>1/</sup> Where two estimates appear, first is for Roan Creek, second for Black Sulfur Creek.

The lack of between-stream variability in this study conflicts with the major conclusion of the first study (above), but this apparent contradiction reflects the choice of streams used in each study. For the oil-shale regions as a whole, the first study clearly indicates that stream drainages can differ; the second study simply shows that of a multitude of possible streams two specific drainages -- Roan and Black Sulfur -- are not geochemically distinct. In fact, the two studies are complementary; the first demonstrates the presence of important betweenstream variability, the second defines the important scales of variability within stream drainages. Attempts to map the geochemical variability of the sediments in these two streams can only be directed to variation at scales greater than 1 km. Mapping at shorter scales may increase the sample load and analytical costs an unbearable amount, and mapping at larger scales will drastically reduce the amount of variation that can be mapped. (Mapping based on 10-km stream segments will not show the variation at the 1-10 km scale because all of that variation is estimated to be at scales less than 10 km.) The minimum number of randomly collect- $\operatorname{ed}$  samples,  $\operatorname{n}_{r}$ , needed to stabilize the mean concentration can be based on the variance ratio of Miesch (1976):

$$v = (P_B + P_{10})/(P_1 + P_{.2} + P_{.02} + P_A)$$
.

where  $P_B$  to  $P_A$  are the percentages of variance estimated for the six levels of the design (table 20). The minimum number of samples,  $n_r$ , required to characterize a 1-km stream segment may be read from graphs in Miesch (1976, p. 9). The number required for a number of elements at two confidence levels is:

nr	Constituents	
	80-percent confidence level	95-percent confidence level
3	Ca, Co, Cr, Cu, Fe, Ga, Mn, Na, Sc, Ti, V	Ca, Cr, Na, Sc
4	The above, plus Al, Ni	The above, plus Co, Cu, Fe, Ga
6	The above, plus Mg	The above, plus Mn, V
7	The above, plus Sr, Y	The above, plus Ti
8	The above, plus Sr	The above
9	The above	The above, plus Ni
<b>1</b> 0	The above	The above, plus Al

Thus, it appears that geochemical mapping within a single drainage should use composite samples of at least seven and perhaps as many as ten samples in each 1-km stream segment. This estimate, together with a need for at least ten such composites to map differences among streams (from the previous study) suggests the probable sampling effort required to adequately map stream-sediment chemistry over the entire oil-shale region.

The occurrence of at least some significant differences between the two streams in this study suggests that geochemical baselines are required for each, at least for those elements judged to be significantly different among streams. For the remaining elements, more stable averages applicable to both streams may be obtained by a "pooled" average based on all the data. The appropriate summaries are given in table 20.

# SPECTROCHEMICAL COMPUTER ANALYSIS by Arthur L. Sutton, Jr.

In an attempt to insure analytical consistency during analysis of rock, soil, and plant material throughout the lifetime of the geochemical survey of the western energy lands, a system of elemental analysis was established near the outset of the work based on the flowchart in figure 42. Descriptions of all methods except that based on emission spectroscopy were described in U.S. Geological Survey (1975, p. 69-81). Analysis of water samples generally follows procedures described in Miesch (1976, p. 18-22).

The "workhorse" of the system outlined in figure 42 is emission spectroscopy by which some 64 elements are looked for simultaneously down to the parts per million level. Of these, 20 to 25 are commonly detected in most samples of a study, and another eight may be measured in a small number of the samples. Most of the initial work of this survey (that undertaken largely in the Powder River Basin of Wyoming and Montana) relied on a visual spectrographic technique described in Miesch (1976, p. 14). Since then, a computerized plate-reading procedure has been instituted for all work of a "background" nature in order to gain a faster, more versatile, and for some elements, a more sensitive analysis.

The analytical procedure is described in Dorrzapf (1973). The recording method as published by Helz (1973) has been replaced with a Hewlett Packard 9601-E Data acquisition system. The following is a list of equipment and Software used for the automatic plate-reading:

32,000-word core storage.
2.47-million word cartridge Disc.
12-bit analog-digital converter.
9-track magnetic tape unit.
Line printer.

The software is described by Walthal (1974) and has been modified to run on the data acquisition system. The new system will be described in a paper in preparation by Catherine Thomas of the U.S. Geological Survey.

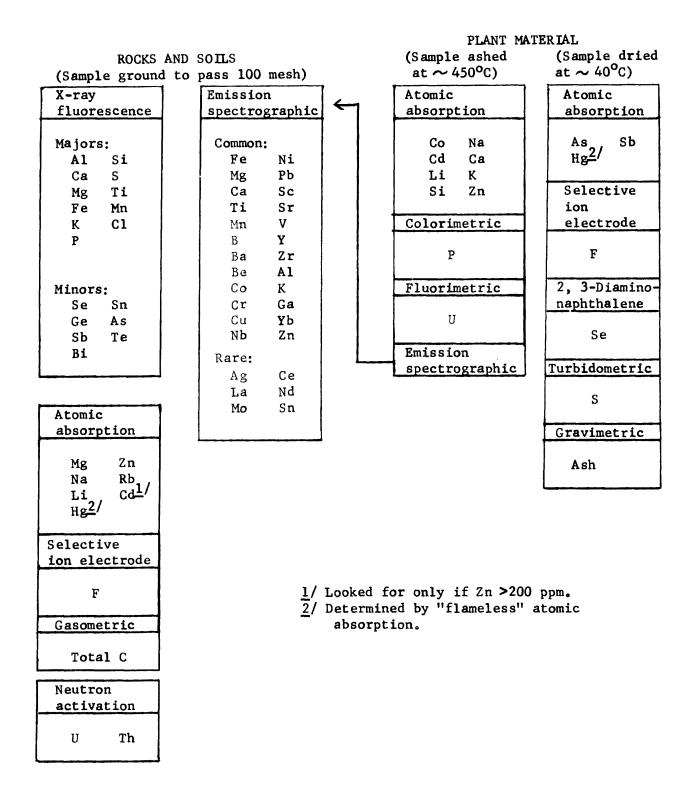


Figure 42.--Methods of total element analysis adopted for rocks, soils, and plants in the geochemical survey of the western energy regions.

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#### UNITED STATES DEPARTMENT OF THE INTERIOR

# U.S. GEOLOGICAL SURVEY Denver, Colorado

#### APPENDICES TO

GEOCHEMICAL SURVEY OF THE WESTERN ENERGY REGIONS (formerly Geochemical Survey of the Western Coal Regions)
Third Annual Progress Report, July, 1976

- APPENDIX I. Probable upper limits of element concentration to be expected in some ordinary landscape materials of the Powder River Basin.
- APPENDIX II. Probable upper limits of element concentration to be expected in some ordinary landscape materials of the Northern Great Plains.
- APPENDIX III. Probable upper limits of element concentration to be expected in some ordinary landscape materials of the Oil Shale Region.
- APPENDIX IV. Toxicity of selected elements to plants, animals, and man-an outline, by Larry P. Gough and Hansford T. Shacklette.
- APPENDIX V. Chemical elements in vegetation and soil near coalfired powerplants, Western Energy Regions.
  - Table 1. Surface and subsurface soil, and sagebrush east of Dave Johnston Powerplant, Wyoming.
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    - 4. Soil and Grass southeast of Four Corners Powerplant, New Mexico.

Open-file Report 76-729 1976

This report is preliminary and has not been edited or reviewed for conformity with U.S. Geological Survey standards or nomenclature.

APPENDIX I

Probable upper limits of concentration to be expected in ordinary landscape materials of the Powder River Basin.

[The limits are estimated as those above which only about one sample in 20 of a randomly selected suite is expected to fall due to natural causes alone. Values expressed as parts per million except as indicated. Limits given to two significant figures except those in parentheses, which are given to only one significant figure because they are judged to be less stable. Leaders (--) indicate insufficient data to estimate limit]

							ĬĀ	Landscape Material $^{1/}$	aterial.							
Property		Rock			So11			Powc	Powder River Sediment	Sedimen	ايد		A	Plant Ash		
	Sha 1e (1)	Shale Sandstone (1) (2)	Surf	Surface	s (5)	Subsurface (6)	(2)	(8)	6	(10)	3	Sagebrush (12)		Lichen (14)	Grass (15)	(16)
A1, 2	;	;	7.3	:	:	7.7	8.2	12	5.6	6.9	(10)	7.6	:	(9)	5.0	:
Sb	:	:	:	(2)	1.8	;	:	;	;	:	;	:	;	:	;	;
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	;	;	;	12	11	:	:	÷	:	;	:	;	;	$1.2^{\frac{2}{2}}$	(2)	:
38	:	;	910	066	1200	890	1000	1400	1400	1500	(1500)	1	1100	710	160	:
30	:	;	:	1.7	1.9	;	:	:	ŧ	:	1.4	:	;	:	:	ł
3	:	;	57	54	20	09	:	25	16	17	96	760	007	1	180	ł
Cd	:	:	:	:	:	:	:	:	;	:	ì	25	16	(6)	2.0	(3)
Ca, 1	:	ł	2.3	ì	:	4.3	11	4.2	3.8	3.0	5.5	:	:	;	6.1	(3)
C(total), 7	5.3	(9)	:	1	:	2.2	3.0	5.6	1.3	1,0	1.8	:	:	;	;	:
Cr	:	:	86	69	11	87	110	(80)	(09)	7.5	190	73	39	29	(70)	;
Co	:	:	16	10	ដ	18	16	11	6.3	4,3	9.6	6.1	5.1	6.5	8.6	3
Cu	1	:	31	8	36	67	06	(05)	56	16	160	:	:		200	:
3 8 7 8 9 9 9 9	:	;	730	:	:	830	840	;	:	ì	:	ŀ	175/	(50) <u>2</u> /	(100) 2/	(9) <sub>7</sub>
Carrente	1	:	20	18	19	ł	56	(56)	11	ង	21	!	:	:	17	:
Ge	ŀ	:	;	2.2	2.0	ŀ	:	;	:	;	;	:	;	;	;	:
I	:	ŧ	:	;	;	;	;	:	ł	;	;	:	;	5.52/	;	:
Fe, X	:	<b>:</b>	3.8	;	:	3.8	5.0	6.1	2.7	2.5	3.9	2.1	:	1.9	2.2	;
[A	;	:	;	:	20	;	180	:	:	:	(100)	:	:	:	:	:
Pb	:	ł	30	21	36	56	23	(20)	ដ	12	i	:	100	(200)	(07)	:
Li	80	25	;	34	41	43	77	(20)	19	17	21	;	22	11	16	(40)
Mg, 7	ŀ	3	1.5	:	;	1.6	4.8	(3)	(.7)	.97	1.2	3.4	:	1.0	1.5	:
Mn	ł	;	830	260	200	07.0	810	480	360	320	(009)	1000	910	009	1300	;
НВ	ì	;	.041	.024	.032	.053	.061	.42	(303)	.046	.047	,037 <u>2</u> 7	.0342/	.132/	(,04) <u>2</u> /	(.01) <sup>2</sup> /
Жотт	ł	;	;	:	:	:	ŀ	;	;	;	:	15	18	;	24	;
NbdN	;	:	;	:	ł	:	:	:	8.1	(19)	18	:	;	:	;	;
NI	:	1	33	77	29	38	67	(30)	n	8.3	16	28	29	17	14	;
, 7, and a second	:	;	:	;	;	:	:	ŀ	;	:	:	2.5	:	ť	1.1	ව
K, 40	:	!	(c)	t i	}	{	<b>(£)</b>	E	2.3	2,5	. 53	ţ	98 8	i h	5,4	92

;	(·s) <sup>2</sup> /	(30)	:	;	$(.3)^{2/}$	:	:	;	$\widehat{\Xi}$	:	:	:	(400)	:	;	;
					$.072^{\frac{2}{2}}$											
:	(.6)2/	(20)	.064	006	$.10^{\frac{2}{4}}$	;	:	.30	5.5	82	:	52	:	110	:	:
}	$2.1^{2/}$	12	.22	1100	$^{16^{\frac{2}{2}}}$	;	;	91.	1.4	. 08	:	:	610	104	:	. 1
;	$1.3^{2/}$	:	:	;	:	:	:	. 29	;	120	:	;	;	;	:	:
(6)	:	:	(.7)	230	;	:	;	(9.)	:	150	<b>E</b>	(46)	88	(4000)	:	:
5.7	:	:	(.7)	(200)	:	:	;	(.3)	:	79	(4)	53	84	(100)	;	;
:	;	:	.68	170	;	:	:	. 16	:	74	3,5	:	26	120	;	:
3.3	;	;	(6.)	310	;	:	:	(2)	;	(200)	(3)	(30)	110	(100)	;	;
20	.58	40	1.01	067	:	:	;	.42	:	170	:	:	120	340	;	:
21	.71	38	06.	350	:	;	;	.39	:	130	;	;	100	340	;	;
15	745	;	;	280	:	15	3.0	:	8.4	150	2.5	27	110	240	:	;
11	(7.)	:	:	300	:	13	3.4	:	4.5	110	2.1	23	91	260	:	0)3/
14	.57	07	.86	230	:	:	;	.39	:	130	;	:	110	0.470	7.38	5
:	;	:	(7.)	:	;	:	;	:	:	:	;	;	:	:	:	:
;	:	:	(7.)	:	;	:	:	:	:	;	:	:	220	;	:	:
ScS	Se	S1, 7	Na, 2	St	S(total), 3		Sherresters	71, 7	r		Yb	Υ	uz	27	р.н	%ad

sources of data (references at end of footnotes): of 44°N. Latitude (USGS, 1976, table 14, figs. 30-31). Identification of landscape materials and (1) Fort Union Formation, outcrops south  $\sim$ 

<sup>0-2.0</sup> cm dopth, <23mm fraction (USGS, 1974, table 1; USGS, 1975, table 1).
0-2.5 cm dopth, <2mm fraction (USGS, 1975, table 1).
15-20 cm dopth, <2mm fraction (USGS, 1975, table 9; Connor, Keith and Anderson, 1976, table 1).
"S-herizon", <2mm fraction (USGS, 1975, table 5).
"C-horizon", <2mm fraction (USGS, 1975, table 5).

<sup>2001-2</sup> mm fraction (USGS, 1976, table 5).
1004-200u Fraction (USGS, 1976, table 5).
6.1 - 1002, 1000 fraction (USGS, 1976, table 5).
6.2 fraction (USGS, 1976, table 5).
6.3 fraction (USGS, 1976, table 5).
6.4 fraction (USGS, 1976, table 1).
6.5 fraction (USGS, 1976, table 1).
6.6 fraction (USGS, 1976, table 1).
6.6 fraction (USGS, 1976, table 1).
6.7 fraction of table 10 fraction (USGS, 1975, table 1).
6.8 fraction of Fourteling (USGS, 1975, table 1).
6.8 fraction of Agroyaron cristatum (USGS, 1976, table 1);
6.7 fraction of Agroyaron cristatum (USGS, 1976, table 11; samples from near Dave Johnston mine only, southern Powder River Basin).

<sup>2/</sup> Determined on drv weight.

<sup>3/</sup> Radioactivity in picocuries/gram. Computed as 4.81(ppm U)+1.1(ppm Th)+8.5(7K). From John Resholt (U.S. Geological Survey, written commun., 1976).

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USGS, 1976, Geochemical Survey of the Western Energy Regions (formerly Geochemical Survey of the Western Coal Regions), Third Annual Trogress Report, July, 1976: U.S. Geol. Survey Open-file Report No. 76-729,138 p.

#### APPENDIX II

# Probable upper limits of concentration to be expected in ordinary landscape materials of the Northern Great Plains.

[The limits are estimated as those above which only about one sample in 20 of a randomly collected suite is expected to fall due to natural causes alone. Values expressed as parts per million (milligrams per liter in water) except as indicated. Limits given to two significant figures except those in parentheses, which are given to only one significant figure because they are judged to be less stable. Leaders (--) indicate data insufficient to estimate limit]

			Lands	cape M	aterial <sup>1/</sup>		
Property	Ro	ock		11	Sediment	Ground	Wheat2/
<u>-</u>	Shale (1)	Sandstone (2)	(3)	(4)	(5)	water (6)	(7)
A1, %			(7)	(8)		79×10 <sup>-7</sup>	••
As							
В			79	91		.91	<del></del>
Ва						.024	
Br						1.1	
C(total), %	5.3		(10)	(6)	(5)		<b></b>
Ca, %			3.5	(15)		(.02)	
Cd							(.1)
C1			- <i>-</i>			.012	
Cr				82			(.03)
Co			11	12			(.06)
Cu			38	35			(5)
F						(4)	(1)
Fe, %			3.7	3.8		.0004	
HCO <sub>3</sub>						1500	
Hg			(.05)	.066			(.01)
K, %			(2)	(2)		.0012	
Li	80	25	33	39	26	. 12	(.2)
Mg, %			1.5	(4)	(2)	(.03)	
Mn			(1000)	(2000)			
Mo							(3)
Na, %			(1)	1.4	(2)	.13	
Ni			30	(40)			(.6)
Pb				30			(.1)
Ra						$2.6^{\frac{3}{2}}$	
Rb	300	98	(100)	(100)	91		

#### APPENDIX II (continued)

## Probable upper limits of concentration to be expected in ordinary landscape materials of the Northern Great Plains.

			Land	scape N	aterial 1/		
Property	Roo	:k		oil	Sediment	Ground	Wheat2/
	Shale (1)	Sandstone (2)	(3)	(4)	(5)	water (6)	(7)
SO <sub>4</sub> , %						(.2)	
Se							(2)
Si, %			(40)	(40)		.0031 <sup>4</sup> /	
Sr			(300)	(400)		(2.3)	
Th			(10)		(10)		
Ti, %			1.2	1.6			
U			(4)	(5)	(6)	(.05)	
V				(100)			(.02)
Zn	220		(100)	87	95	(.9)	(50)
Rad <sup>5</sup> /			<b>(</b> 50 <b>)</b>				
			In wat	er only	7		
<b>Al</b> kalinity						(1000)	
Dissolved soli	ds (180	°C)				3000	
Hardness (Tota	1 as Ca	CO <sub>3</sub> )				(2000)	
Temperature, °	С					14	
pH (standard u	nits)					8.9	
Gross B						15 <sup>3</sup> /	
Specific condu	ctance,	micromhos/c	m			(4000)	
Sodium absorpt	ion rat:	io				(100)	

<sup>1/</sup> Identification of landscape materials and sources of data (references at end of footnotes).

## References:

Shacklette, H. T., Erdman, J. A., Harms, T. F., and Papp, C. S. E., 1976. Trace elements in plant foodstuffs in Ochme, F. W., ed., Toxicity of Heavy Metals in the Environment: Marcel Dekker, New York (in press).

USGS, 1976, Geochemical Survey of the Western Energy Regions (formerly Geochemical Survey of the Western Coal Regions), Third Annual Progress Report, July, 1976: U.S. Geol. Survey Open-file Report No. 76-729, 138 p.

<sup>(1)</sup> Fort Union Formation, outcrop (USGS, 1976, table 14).

<sup>(2)</sup> Do

<sup>(3) &</sup>quot;A-horizon", <2mm fraction (USGS, 1976, table 9, figs. 15-27). (4) "B-horizon", <2mm fraction (USGS, 1976, table 9, figs. 15-27).

<sup>(5) &</sup>lt;150μ fraction (USGS, 1976, table 3).

<sup>(6)</sup> From domestic or livestock wells, average depth 30m (USGS, 1976, table 13).

<sup>(7)</sup> Grains of Triticum aestivum and T. durum (Shacklette and others, 1976).

<sup>2/</sup> Determined on dry weight.

<sup>3/</sup> Radioactivity in picocuries per liter.

As SiO<sub>2</sub>.

Radioactivity in picocuries/gram. Computed as 4.81(ppm U)+1.1(ppm Th)+8.5(%K). From John Rosholt (U.S. Geological Survey, written commun., 1976).

#### APPENDIX III

Probable upper limits of concentration to be expected in ordinary landscape materials of the Oil Shale Region [The limits are estimated as those above which only about one sample in 20 of a randomly collected suite is expected to fall due to natural causes alone. Values expressed as parts per million except as indicated. Limits given to two significant figures except those in parentheses, which are given to only one significant figure because they are judged to be less stable. Leaders (--) indicate data insufficient to estimate limit]

		Landscape	material1/	
Property	Soil, Piceance Creek Basin	Sedi	ments	Sagebrush ash, Green River Basin
	(1)	(2)	(3)	(4)
A1, %	7.0		(8.0)	4.7
As	19	20		.64 <u>2</u> /
В	(100)	(70)	(65)	(260)
Ва	2,200	(1,000)	1,300	670
Be	(4)	5.9	• •	
C (total), % -	6.9	(6)		
Ca, %	(9)	(10)	9.2	13
Cd	<b></b>			6.7
Со	15	(10)	14	4.6
Cr	(100)	130	180	34
Cu	(60)	33	27	160
F	830	30	• •	332/
Fe, %	(3)	(4)	3.5	1.4
Ga	(40)	(30)	(23)	
Ge	2.1			
Hg	.17			.0342/
K, %	3.2	(3)	3.6	36
La			<b></b>	
Li	(70)	(60)		27
Mg, %	(2)	(2)	1.9	(2)
Mn	650	(500)	400	<b>7</b> 50
Мо	14	••		14
Na, %	3.2	(4)	(3)	. 54

#### APPENDIX III -- Continued

Probable upper limits of concentration to be expected in ordinary landscape materials of the Oil Shale Region

		Landscape m	aterial1/	
Property	Soil, Piceance Creek Basin	Sedime	nts	Sagebrush ash, Green River Basin
	(1)	(2)	(3)	(4)
Nb	12	(18)		
Ni	48	100	(24)	21
P, %		.10		4.8
Pb	59	(20)	26	73
Rb	160	46 10		
S (total), % -		<b></b>		.212/
Sb	1.7	<b>-</b>		
Sc	12	(20)	13	·
Se	.59			
Sn	3.0			.072 <sup>2</sup> /
Si, %	(30)			19
Sr	510	(700)	560	770
Ti, %	(.4)	.049	.42	.17
U				1.5
V	100	(100)	110	64
Υ	(20)	(40)	30	
Yb	(6)	(4)	2.9	
Zn	(100)	660		560
Zr	410	(400)	390	130

<sup>1/</sup> Identification of landscape materials and sources of data (references at end of footnotes):

## References:

<sup>(1)</sup> Bulk surface soil (U.S. Geol. Survey, 1976, tables 15, 16).

<sup>(2) &</sup>lt;150μ fraction (U.S. Geol. Survey, 1976, tables 18, 19).</li>
(3) <150μ fraction (U.S. Geol. Survey, 1976, table 20).</li>

<sup>(4)</sup> Unwashed Artemisia tridentata (U.S. Geol. Survey, 1976, table 7).

<sup>2</sup>/ Determined on dry weight.

U.S. Geological Survey, 1976, Geochemical Survey of the Western Energy Regions (formerly Geochemical Survey of the Western Coal Regions), 3rd Ann. Progress Report, (July, 1976): U.S. Geol. Survey Open-file Rept. No. 76-729, 138 p.

## APPENDIX IV

## TOXICITY OF SELECTED ELEMENTS TO PLANTS, ANIMALS, AND MAN--

AN OUTLINE

Ву

Larry P. Gough and Hansford T. Shacklette

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Toxicity of selected elements to plants, animals, and man--

an outline

By
Larry P. Gough and Hansford T. Shacklette

## Introduction

Investigators have long recognized the importance of certain elements, commonly called "minerals," in the diet of humans and animals and in the soil that supports plants, in that these elements are essential for the life or optimum health of the organisms. Deficiencies of 20 to 24 elements in animals and man (Frieden, 1972) and of 13 to 18 elements in plants (Epstein, 1965) have been recognized. At the same time, an understanding of the responses of these organisms to the insult of toxic concentrations of these and other elements also has been of interest. More recently, concern has arisen with the effects of an organism's exposure to the more subtle chronic and subchronic concentrations of certain elements that industrial and other human activities are releasing into the environment.

Many studies of element toxicities have been made, and reports of these studies are scattered through the biological, medical, geological, and other literature. The present Government requirement for preparing environmental impact statements before certain types of industrial and other operations are undertaken necessitates judgments to be made regarding the potential health effects, if any, of elements that may be released into the environment by these operations. Although this judgment may be outside the fields of the physical and biological scientists who must predict environmental impacts, certain valid estimations can be made if adequate information is available. The purpose of this outline is to provide some specific data on the known toxicity levels of selected elements that may reach potentially dangerous concentrations in the environment. We have limited our concern to toxic levels in organisms that are acquired through absorption, ingestion, and inhalation; intravenous, subcutaneous, intramuscular, or intraperitoneal injections of toxic elements can hardly be considered of "environmental" concern.

Much has been written on the toxicities of some elements such as lead, mercury, and selenium, and our chief task with these elements was that of selecting the most useful reports to include. For some other elements, reports of toxicities are few and are often in obscure publications. The elements selected for this outline are those which may be environmentally important and for which quantitative data are available. This list of toxic elements obviously is incomplete—for example, uranium is often cited as being toxic to organisms (due to ionizing radiation), but we have no quantitative confirmation of this effect under natural conditions. Some of the information in this outline is from unpublished data in our files; most statements, however, are identified by reference citations.

The outline format that is used presents the elements alphabetically by their common English names. We have divided the notes on each element into three parts--plants, animals, and man--followed by associated toxicities under natural and man-induced conditions, where appropriate.

Concentrations of elements generally are presented as parts per million (ppm), although other methods of expressing concentrations may be quoted. In some instances units such as mg/kg of body weight,  $\mu$ moles/1,  $\mu$ g/m³, or percent provide a clearer concept for a given example, and converting them to ppm was either impossible or considered to be unnecessary.

It will be noted in this report that many of the elements that are discussed are essential for plants or animals, yet are toxic under certain conditions. The toxicity of an element depends, first of all, on its chemical form. For example, chlorine in the elemental form (a gas) is highly toxic, whereas chlorine compounds may be harmless, as is sodium chloride (common salt). Conversely, elemental arsenic is not toxic, although many arsenical compounds are highly toxic. Many reports do not specify the chemical form of an element when discussing its toxicity. It can be assumed for most of these reports that, under the specified natural or experimental conditions, the element existed in an undetermined compound, and that only the total concentration of the element was known. In most reports in which the basis for expressing concentrations of an element in plant or animal tissues is not specified, a dry weight basis can be assumed.

The toxicity of a substance is also determined by the dosage—that is, the amount (in relation to body weight), and the frequency and duration of administering the substance to the organism. The duration of specified dosages of toxic elements was not given by Bowen in his 1966 report. In reports that relate toxicity to body weight of the experimental animals, "live" or "wet" weight is commonly used. Amounts of an element in relation to body weight are expressed as ingested amounts. The term "LD<sub>50</sub>" means that the specified dose is lethal to 50 percent of the experimental organisms. Quantities of total diets given are based on a one-day consumption, unless otherwise states.

To be toxic, an element must be "available" to the plants or animals—that is, it must exist in a form that can enter tissues of the organism, either in solution (generally aqueous), as a gas, or (uncommonly) as a solid, or it must emit ionizing radiation. Fotal amounts of a toxic element in the environment are not relevant to an adequate estimation of the toxicity hazard unless it can be shown that the element exists in, or is likely to assume, an available form under the environmental conditions in which it occurs.

## Aluminum (non-essential to plants and animals)

#### Plants--

Under natural conditions

Because aluminum is abundant in most soils, toxicity is largely dependent on the exchangeable amount present due to low soil pH. Only small quantities of soluble aluminum were found by Magistad (1925) in soils with pH values between 4.7 and 7.8. In naturally acid soils, Pierre, Pohlman, and McIlvaine (1932) reported the following pH-soluble aluminum relationships: pH 4.0, 1.5-23 ppm; pH 4.5, 0-12 ppm; and pH 4.9, 0-2 ppm. Because of aluminum toxicity, certain crops cannot be grown on some naturally acid soils without applications of lime. In contrast, some plants are known as "aluminum accumulators" and may contain as much as 37 percent aluminum in ash.

Under man-induced conditions

Susceptibility to aluminum poisoning differs widely among plant species. McLean and Gilbert (1927) classified 12 crop plants according to their sensitivity to aluminum in culture solutions as follows: sensitive (depressed by 2 ppm aluminum), barley, beet, lettuce, and timothy; intermediate (depressed by 7 ppm), cabbage, oats, radish, rye and sorghum; and tolerant (depressed by 14 ppm), corn, redtop, and turnip. Acidic mine spoil and drainage waters may be suspected of causing aluminum poisoning in some native and cultivated plants.

#### Animals --

Under natural dietary conditions

We have no reports of animal toxicity attributed to naturally occurring aluminum in the environment. Several investigators have reported that aluminum is a specific root poison for many species, and that the poisoned roots are unable to translocate the element to other parts of the plant (Pratt, 1966a), therefore there seems to be little likelihood that grazing animals are affected by these plants. On the other hand, sweetleaf (Symplocos tinctoria), an aluminum accumulator (Robinson and Edgington, 1945), is a preferred browse shrub for horses and cattle (Small, 1933), yet no toxicity symptoms in these animals have been reported as due to aluminum. However, Hutchinson (1943) concluded that this plant, reported to contain 2.41-3.45 percent aluminum in dry matter, could not constitute the sole diet of these animals because of the inhibitory effect of aluminum on phosphorus metabolism.

Under man-induced dietary conditions

Bowen (1966) listed 200 mg Al<sup>3+</sup> in a 10 g/day dry weight diet (20,000 ppm) as being toxic to rats, whereas 220 mg (22,000 ppm) was lethal.

#### Man-

Aluminum poisoning in humans appears to be rare. Dr. Carl J. Marienfeld (oral commun., 1973) reported a case of a woman suffering aluminum poisoning because of having eaten, over a prolonged period of time, acidic foods that had been wrapped in aluminum foil. We have found, by experiments, that tomato fruits will dissolve aluminum foil, even at a

temperature of 0°F. Smith (1928) reported that ingestion of 150 mg aluminum per day is without obvious effects on normal humans; 200 mg may, however, give rise to mild catharsis, which increases with the dose. Regarding absorption of inhaled airborne aluminum, Hutchinson (1943, p. 252) wrote, "The fact that all investigators have found aluminum in the bile indicates that some of the aluminum present in the faeces, as well as in the urine, has been involved in a metabolic cycle. It is conceivable that this aluminum has in part entered the blood stream through the pulmonary epithelium, but if such a mode of entry were generally important significant negative balances would have been reported wherever balance sheets have been made." A number of observations indicate that high concentrations of aluminum may be toxic to the nervous system (Crapper and others, 1973). These authors analyzed the brains of persons who died with Alzheimer's disease (a disease occurring after the age of 40 and producing progressive dementia) and found concentrations of aluminum similar to those in the brains of experimental animals that had been injected with 150-225 ug aluminum. as aluminum chloride, and as a result had developed neurological symptoms similar to those of Alzheimer's disease in humans.

## Arsenic (non-essential to plants and animals)

#### Plants--

Under natural conditions

Although the free element is not considered poisonous, many of its compounds are extremely so (Liebig, 1966). Brooks (1972) stated that the toxicity of this element to plants was severe. The arsenic in normal soils ranges from <1 to 40 ppm (Underwood, 1971); within this range, damage to plants is not expected, and the arsenic content of most species is low (<10 ppm, dry weight). Soils in the vicinity of some heavy metal deposits may contain much more arsenic, and douglasfir (Pseudotsuga menziesii) growing in such soils may contain as much as 8,200 ppm in ash (Warren and others, 1968).

Under man-induced conditions

The toxicity to plants of certain arsenic compounds, principally sodium arsenite and arsenic trioxide, is so great that these compounds were used as herbicides for many years. Arsenic compounds such as calcium arsenate, lead arsenate, and cupric arsenite (Paris green) formerly were widely used as insecticides. The long-term use of these materials in agricultural practice accounts for most recorded cases of plant toxicities. The toxicity depends on the concentration of soluble, not total, arsenic in soils. Studies of unproductive old orchard soils in the Yakima Valley from which apple trees had been removed revealed 3.4-9.5 ppm of readily soluble arsenic in the top 6 inches of soil. Damage to alfalfa and barley was proportional to the concentration of soluble arsenic; if above 2 ppm, marked damage to the plants occurred (Vandecaveye and others, 1936). Arsenic is introduced into the environment as an air pollutant from burning coal, and from smelters and refineries (Underwood, 1971), but we have no reports of damage to plants from these sources.

#### Animals--

Under natural dietary conditions

Examples of toxicity of arsenic to animals under natural conditions are believed to be uncommon. Grimmett (1939) investigated livestock poisoning in a valley of New Zealand and found soils and muds contained as much as 1.9 percent arsenic; water from springs, streams, and surface depressions varied from a trace to 13 ppm of arsenic; and pasture grasses contained 2.8 to 6.9 ppm (dry weight) arsenic. He concluded that the danger to stock was not from the arsenic in the forage, but from that in the mud or water which might be ingested. Under man-induced dietary conditions

There is probably little danger of arsenic poisoning from feeding plants and plant products to animals. In fact, four organic arsenic compounds (arsenilic acid, 4-nitrophenylarsonic acid, 3-nitro-4-hydroxyphenylarsenic acid, and arsenobenzene) are used as growth stimulants for pigs and poultry (Underwood, 1971). Trivalent compounds (arsenites) are far more toxic than the pentavalent forms (arsenates). The 96-hour LD50 for mice and rats is 11.2 ppm arsenite in the diet whereas it is 112 ppm for arsenate. Schroeder and Balassa (1966) reported that arsenic deactivates enzymes with thiol groups and acts as an antagonist of iodine and selenium.

#### Man--

Under natural dietary conditions

Water is the most common natural material causing arsenic poisoning. Amounts in excess of 0.05 mg/l in drinking water constitute grounds for rejection (U.S. Public Health Service, 1961). Wyllie (1937) reported illness and one fatality in a farm family that used water from a deep well having 0.4-10 ppm arsenic (as As203). Large beds of FeAsS occurred about 10 miles from this well. Water from shallow wells near this farm were free of arsenic. Borgono and Greiber (1971) reported that prolonged consumption (12 years) of water high in arsenic (0.8 ppm) produced cutaneous lesions in over 30 percent of the inhabitants of a city in Chile. Foods of plant origin contain so little arsenic that toxicity to humans in unlikely. Seafood of marine origin contains much more arsenic--maximum values reported (fresh weight basis) follow: Oysters, 10 ppm; mussels, 120 ppm; prawns, 174 ppm; and shrimp, 42 ppm (Underwood, 1971). This author stated further that the amounts of arsenic ingested daily in the food are greatly influenced by the amounts and proportions of seafoods included in the diet.

#### General notes on toxicity

Elemental arsenic is not toxic (Schroeder and Balassa, 1966), whereas most compounds of this element are highly toxic (Stecher, 1968). Schroeder and Balassa (1966) reported that mountaineers in Syria and the Alps have been known to consume large quantities of native arsenic ("arsen"), believing that it promotes endurance at high altitudes. The minimum fatal dose of arsenous oxide for man was given as 0.06-0.18 g by Monier-Williams (1950). This author also stated that the British Royal Commission set maximum limits of

1.4 ppm arsenic for solid foods, and 0.14 for liquid foods, including beverages. This limit for foods seems unrealistic, in view of the arsenic content of seafoods listed above. Thomas (1973) gave 5-50 mg/kg body weight as the probable lethal dose for an adult, whereas Bowen (1966) listed as toxic 5-50 mg AsIII or AsV in a 750 mg/day dry weight diet (7-67 ppm) and as lethal, on the same basis, 100-300 mg (133-400 ppm).

## Boron (essential only for higher plants)

#### Plants--

Under natural conditions

The difference between required amounts of boron and toxic amounts is very small--commonly 1-2 ppm in soil. Analysis of total soil boron is not very useful in predicting toxicity; the boron may be held in relatively insoluble compounds such as tourmaline, or in organic residues or marine sediments where it is more readily available. The amount of water-extractable boron in soil is a good index of essential or toxic levels (Bradford, 1966a). For example, for orchard trees extractable boron in the range of 0.5-1.0 ppm promotes normal growth, whereas values above 1.0 ppm are high, and values above 2.0 ppm indicate possible toxicity (Sauchelli, 1969). Boron tolerance varies widely among plant species; examples of this range of tolerance follow: sensitive--lemon and other citrus trees, peach, navy bean, and pecan; semitolerant--lima bean, tomato, corn, wheat, and cotton; tolerant--carrot, lettuce, onion, alfalfa, beet, and asparagus.

Under man-induced conditions

Because the difference between essential and toxic amounts is so small, most cases of toxicity are caused by excessive amounts applied in fertilizers. Toxic amounts may also be introduced in irrigation water. Where the boron content of water is 0.10 to 0.20 ppm or more and one acre-foot (or more) of water is used, boron deficiency is unlikely. But if the boron content of the water is greater than 0.75 ppm some sensitive crops will begin to show toxicity symptoms (Bradford, 1966a).

#### Animals ---

Under natural dietary conditions

Underwood (1971, p. 434) stated, "Boron intakes by grazing animals must be very variable, depending upon the soil type and on the plant species consumed, because the boron concentrations are influenced by the species and the boron status of the soil. These intakes would invariably be much higher, per unit of body weight, than those of humans consuming mixed diets containing a substantial proportion of foods of animal origin." The pastures of solonetz and solonchak soils of the Kulundinsk steppe in Russia were reported by Plotnikov (1960) to be so high in boron that gastrointestinal and pulmonary disorders occur in lambs. Moreover, the water supplies were unusually high in boron (0.2-2.2 mg/1), which probably contributed to the boron toxicity.

#### Man--

Underwood (1971, p. 434) stated, "The boron in food, and boron added as sodium borate or boric acid, is rapidly and almost completely absorbed and excretee, largely in the urine. Where high intakes occur either accidentally or from the treatment of large burns with boric acid, similar high absorption and urinary excretion take place, but sufficient boron may be temporarily retained in the tissues, especially in the brain, to produce serious toxic effects." Bowen (1966) listed as toxic 4,000 mg boron (borate) in a 750 g/day dry weight diet (5,300 ppm).

## Bromine (non-essential for plants and animals)

#### Plants--

Under natural conditions

The bromine content (principally as bromides) in normal soil is so low, ranging from 10 to 40 ppm, that bromine toxicity has not been a problem in crop production in the past (Martin, 1966a).

Under man-induced conditions

Most cases of bromine toxicity to plants are related to residual bromine in the soil following fumigation with bromine compounds (principally ethylene dibromide and methyl bromide). However, the possibility exists of bromine contamination of soils by motor vehicle and industrial emissions. In land plants bromine normally ranges from trace concentrations to about 260 ppm in the dry tissue. It is especially high in melons, carrot tops, celery tops, and mushrooms. In contrast to land plants, marine plants contain up to about 2,000 ppm (Martin, 1966a). Plant species differ greatly in their tolerance to soil bromine; onion is so sensitive that it has been used as a test plant for detecting soil bromide (O'Bannon, 1958). Other sensitive plants include bean, beet, cabbage, celery, citrus, pea, peanut, pepper, potato, spinach, sugar beet, sweet potato, and turnip. The bromine content of dry leaf tissue has been used as an indication of toxicity; for example, leaf bromine concentrations in citrus seedlings of 0.17, 0.33, 0.4, 1.3, and 1.8 percent were associated with 12, 22, 31, 57, and 90 percent reduction in growth, respectively (Martin and others, 1956). Concentrations of watersoluble soil bromine were reported to have the following effects: 38-83 ppm, reduced growth of bean and cabbage; 26-53 ppm injured carnation plants; 15 ppm reduced growth of citrus seedlings, and 600 ppm almost killed the plants; and growth of beans was greatly retarded by 300 ppm (summaries given by Martin, 1966a).

## Animals--

Under natural dietary conditions

Although the bromine content of animal tissues and milk is greatly influenced by the bromine in the feeds, we have no reports of bromine toxicity from feed sources.

Under man-induced dietary conditions

Bowen (1966) listed as lethal to rats 800 mg Br<sup>-</sup> in a 10 g/day dry weight diet (80,000 ppm).

#### Man--

Dietary bromine is retained for only short periods in the tissues and is excreted mostly in the urine. Underwood (1971, p. 435) stated, "Human dietary bromine intakes have probably increased in recent years in areas where organic bromides are used as fumigants for soils and stored grains, and in motor fuels." However, there appear to be no toxicity problems associated with this intake. Thomas (1973) gave 500-5,000 mg/kg body weight of bromides (sodium, potassium, ammonium, and others) and 50-500 mg/kg body weight of bromate salts as the probable lethal oral dose for an adult.

## Cadmium (non-essential for plants and animals)

#### Plants--

Under natural conditions

No toxicity has been demonstrated. Cadmium is a relatively rare element that is rather uniformly distributed in the most abundant rocks of the earth's crust, which has an average content of 0.15-0.2 ppm (Fleischer and others, 1974). The only natural concentrations of commercial importance are those in sulfide deposits, especially those containing zinc, lead, and copper, and the toxicities of these elements in the deposits is most likely more severe than that of the low concentrations of the cadmium.

Under man-induced conditions

Brocks (1972) stated that the general toxicity of this element to plants was moderate. Allaway (1968) reported that 3 ppm cadmium in the tissue of plants depressed growth. Cadmium was reported to reduce plant growth at the following nutrient solution concentrations: 0.2 ppm--beets, beans, and turnips; 1 ppm--corn and lettuce; 5 ppm--tomato and barley; 9 ppm--cabbage (Page and others, 1972). Traynor and Knezek (1973) reported that corn grown on cadmium-enriched soils readily absorbed and translocated the element. They also found growth reduction in corn at its maximum when 281 ppm cadmium was added to the soil resulting in a plant concentration of 131 ppm (ash weight basis). The concentrations of cadmium in soils required to damage plants were higher than even those in soils of contaminated areas (Fleischer and others, 1974).

#### Animals--

Under natural dietary conditions

The cadmium content of plants under natural conditions is low (Shacklette, 1972), and various animal studies have suggested that the absorption of cadmium from the gastro-intestinal tract is poor (Fleischer and others, 1974), therefore poisoning of animals is unlikely.

Under man-induced dietary conditions

Mammals have no effective mechanism for the elimination of ingested cadmium; with time it tends to accumulate in the liver and kidney. Its relative toxicity to mammals has been rated from moderate to high (Allaway, 1968). Cadmium from industrial or vehicular pollution can be absorbed by plants, or deposited on plant surfaces, to the

extent that the plants are toxic to animals. For example, Goodman and Roberts (1971) reported grass that was contaminated by industrial pollution contained 9.9 ppm cadmium, whereas control samples of the grass contained only 1 ppm; this contaminated grass caused the death of a horse (but the immediate cause of death was attributed to plumbism). They found contaminated grass to contain as much as 40 ppm cadmium in ash. Cadmium was suspected of killing a horse which contained 80 ppm cadmium in its liver and 410 ppm in its kidneys (Lewis, 1972). Thirty to sixty ppm cadmium in the diet of sheep for 191 days was shown to reduce growth and feed intake (Doyle and others. 1972). Forty-five ppm cadmium in the diet of rats for 6 months caused slight toxic symptoms (Underwood, 1971). Bowen (1966) stated that 0.5 mg/day Cd<sup>2+</sup> in a total dry weight diet of 10 g (500 ppm) is toxic to rats, whereas 16 mg/dav (1,600 ppm) is lethal. A subtoxic level of 5 ppm cadmium in the drinking water of rats, given for 180-240 days, produced systolic hypertension. It has been used as an anthelmintic drug in swine and poultry at concentrations ranging from 30-1,000 ppm in the diet (Stecher, 1968). Cadmium appears to be highly toxic to aquatic organisms at low concentrations, as follows: lethal to the flatworm Polycelis nigra at 2.7 ppm; to sticklebacks at 0.2 ppm; to goldfish at 0.02 ppm; to Daphnia magna at 0.003 ppm (Schroeder and Balassa, 1961a).

#### Man--

Under normal environmental conditions

The normal cadmium content of food plants is low, ranging from 0.1 to 1 ppm in dry material (Shacklette, 1972), therefore poisoning from this source is unlikely.

Under the effects of environmental pollution by cadmium The first likely instance of cadmium poisoning in man due to general environmental contamination is that of itai-itai disease in the elderly women who lived in the vicinity of a mine in Japan. It was demonstrated that the water, rice, and fish in the endemic area contained high concentrations of cadmium and other metals, probably due to contamination of the local river by the effluent from a zinclead-cadmium smelter (Fleischer and others, 1974). Bowen (1966) stated that the normal dietary intake of Cd2+, based on a total dry weight diet of 750 g/day, is 0.6 (0.8 ppm), whereas 3 mg/day (4 ppm) is toxic. A recent study of the environmental impact of cadmium (Fleischer and others, 1974) concluded, "Based on present knowledge, and there are many gaps, there is no solid evidence of a hazard to the general population from cadmium in food, air, or water. Contamination of food and water rather than air would seem to present more of a potential problem. This might not be the case with smoking or excessive occupational exposures."

## Chlorine (essential for plants and animals)

#### Plants--

Under natural conditions

The chloride ion is itself toxic if too greatly concentrated, also the common natural chlorine compound, sodium chloride, is toxic through its effect on osmotic pressure within the plant, if too concentrated. Symptoms of excess chloride include burning and firing of leaf tips or margins, bronzing, premature yellowing and abscission of leaves and, less frequently, chlorosis (Eaton, 1966). Within the concentration ranges of sodium chloride tolerated by a species of plant, for each increase in the osmotic pressure of the substrate solution there is an increase in the osmotic pressure of the plant sap; beyond this range, lethal wilting occurs. Under natural conditions, areas inundated by sea water, or strongly influenced by sea spray, may accumulate toxic amounts of sodium chloride in the soil. Evaporative salt in closed geographic basins may also reach toxic concentrations. On natural undrained soil in Australia the chloride in leaf petioles of grape (percent, dry matter) related to leaf toxicity symptoms were as follows: 0.81, no toxicity; 1.35, slight burning; 1.55, burning; 2.50, severe burning (Woodham, 1956).

#### Under man-induced conditions

Chloride toxicity may be produced in plants by over-fertilizing, such as with potassium chloride. Chloride toxicity may also result from irrigation with slightly salty water with insufficient flushing of the soil. Plants range widely in their resistance to toxicity from the halophytes such as asparagus, to highly sensitive species. Experimental studies with grapefruit in which the trees were watered with different levels of salt concentration in the water gave the following results (Pearson and others, 1957): 300 ppm salt, relative weight of tops was 100, 0.07 percent (in dry matter) in leaves; 1,300 ppm salt, relative weight of tops was 46, 1.28 percent in leaves; and 2,300 ppm salt, relative weight of tops was 38, 1.35 percent in leaves. The two higher concentrations produced defoliation, dieback, chlorosis, bronzing, and burning.

#### Animals --

Under natural dietary conditions

Forage plants in general are so low in chlorine that salt must be provided to herbivorous animals; therefore, natural chlorine toxicity in these animals is very unlikely.

Under man-induced dietary conditions

Our only report is one given by Bowen (1966) who listed as lethal to rats >900 mg Cl in a 10 g/day dry weight diet (90,000 ppm).

#### Man \_\_

We have no reports of human toxicity attributed to excessive chlorine in the natural environment, although of course chlorine gas is highly toxic to plants, animals, and man. Thomas (1973) gave 50-500 mg/kg body weight as the probable lethal dose of chlorate salts for an adult.

Chromium (non-essential for plants, essential trace element for animals)

#### Plants--

#### Under natural conditions

The growth of only certain species on "serpentine soils" has commonly been attributed to the high chromium levels in such soils (Brooks, 1972), but excessive nickel, unfavorable Mg:Ca ratios, and deficiency of molybdenum may also contribute to this condition (Vanselow, 1966a). Soil from "poison spots" in Oregon contain as much as 2-3 percent chromic oxide (McMurtrey and Robinson, 1938).

#### Under man-induced conditions

Brooks (1972) reported chromium toxicity to plants as severe, whereas Allaway (1968) stated it to be moderate. Chromium in the form of chromates is particularly toxic (McMurtrey and Robinson, 1938). In soil, 1,370-2,740 ppm chromium caused chlorosis in citrus; 10-15 ppm chromium (as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in the nutrient solution was toxic to barley (Mertz, 1974a). In corn leaves, 4-8 ppm (dry weight basis) chromium was toxic (Soane and Saunder, 1959).

#### Animals--

#### Under natural conditions

Underwood (1971, p. 263-264) stated, "Chromium, particularly trivalent chromium, has a low order of toxicity. A wide margin of safety exists between the amounts ordinarily ingested and those likely to induce deleterious effects."

#### Under man-induced dietary conditions

The hexavalent form of chromium may be 100 times more toxic than the trivalent form; however, both are relatively nontoxic to mammals and other vertebrates (Schroeder, Balassa, and Tipton, 1962a). Underwood (1971) stated that 50 ppm chromium in the diet resulted in growth depression of experimental animals. Thirty to forty mg/kg of body weight as zinc chromate is lethal to calves within one month, and about 20 times that amount is lethal to cows. Thirty ppm chromium in the liver is diagnostic of chromium toxicity (A. A. Case, written commun.). Five mg chromate in a 10 g/day dry weight diet (500 ppm) is toxic to rats. Chromium is potentially carcenogenic (Bowen, 1966).

#### Man--

The lung is the only organ that appears to accumulate chromium, and this may be related to airborne exposure to chromium-containing dust (Mertz, 1967). Bowen (1966) reported that in a 750 g dry weight diet, normal consumption of chromate is about 0.05 mg (0.07 ppm), whereas the toxic level is 200 mg (270 ppm) and the lethal level is 3,000 mg (4,000 ppm). Schroeder, Balassa, and Tipton (1962a) reported that consumption of water containing 1.0-25 ppm chromium by a family over several years produced no apparent ill effects. They further stated that chromium is one of the least toxic of trace metals.

Cobalt (essential trace element for blue-green algae and nodule bacteria, non-essential for higher plants although growth and yield increases have been reported; essential trace element for animals)

#### Plants --

Under natural conditions

Vanselow (1966b) reported that cobalt exhibits toxicity to plants when the amounts available to the plant exceed certain low levels, but that a naturally occurring excess of cobalt in soils is improbable and that no instances so far had been noted. Plant species range widely in their content of cobalt, yet show no toxicity symptoms. Some trees have very high concentrations in their leaves, as for example, black gum (Nyssa sylvatica) leaves were reported to contain as much as 10,000 ppm in ash, and persimmon (Diospvros virginiana) leaves 2,000 ppm; most other species contain much less (Connor, Shacklette, and others, 1975).

Under experimental conditions

A number of authors (see Vanselow, 1966b) have reported that in solution cultures small amounts of cobalt, sometimes as low as 0.1 ppm, produced adverse or toxic effects on many crop plants. The symptoms of cobalt excess include depressed growth, chlorosis, necrosis, and even death of the plant. The chlorosis is frequently described as resembling that of iron deficiency (Vanselow, 1966b). Sudan grass containing 19-32 ppm (dry weight basis) cobalt showed toxicity symptoms when grown in soils to which 2,000 pounds of cobalt per acre had been added (Fujimoto and Sherman, 1950).

#### Animals--

Under natural dietary conditions

We have no reports of cobalt toxicity attributed to consumption of natural feedstuffs; pasturage deficiency in cobalt is of far greater concern than are potentially toxic concentrations in plants.

Under man-induced dietary conditions

Cobalt is relatively non-toxic. Sheep can tolerate large doses of cobalt; 0.35/100 kg/day produced no ill effects (Becker and Smith, 1951). Smith (1962) listed the following in mg/kg body weight/day: rats-2.5, non-toxic; dogs-10, non-toxic; sheep-3, non-toxic; and cattle-about 1, toxic. Bowen (1966) listed as toxic to rats 0.7 mg Co<sup>2+</sup> in a 10 g/day dry weight diet (70 ppm).

## Man--

The edible parts of food plants contain only <1-10 ppm (ash basis) cobalt, therefore toxicity attributed to this source is very unlikely (Connor, Shacklette, and others, 1975). As with animals, the toxicity of non-radioactive isotopes of cobalt are of little importance. At a time when cobalt was used in beer in order to preserve the foam, it was suspected of causing the "beer drinkers cardiomyopathy" syndrome. Some evidence (Burch, Williams, and Sullivan, 1973), however, implicates selenium in conjunction with cobalt as being responsible. Bowen (1966) listed as toxic 500 mg Co<sup>2+</sup> in a 750 g/day dry weight diet (670 ppm).

## Copper (essential trace element for plants and animals)

#### Plants--

Under natural conditions

Soil influenced by a high degree of copper mineralization may be toxic to native or cultivated plants. Fraser (1961) reported that large trees were absent, and tree seedlings were killed, in a syngenetic copper deposit in a swamp in New Brunswick, and that muck from this swamp killed cucumber plants to which it was applied. There are many reports in the literature of copper toxicity to plants on or near copper deposits, and the degree of resistance to copper toxicity by different species has been used as a geobotanical method of mineral exploration.

Under man-induced conditions

Copper sulfate (blue vitriol) has been used for over seventy years as an algicide at an achieved concentration of 1 mg/1 (1 ppm) for the upper 0.5 m of water (Mackenthun and Ingram, 1967). Most copper toxicities in crop plants have been caused by the use of Bordeaux mixture (copper sulfate and lime) as a fungicine. Toxicity to copper in plants is usually manifested by chlorosis (yellowing) of the foliage, caused by the interference of excessive copper with iron metabolism in the plant. Reuther and Smith (1953) found appreciable chlorosis of citrus seedlings occurring when the total copper of a very sandy soil of pH 5.0 or below exceeded 150 ppm. Westgate (1952) reported copper toxicity in several crops on old vegetable fields having over 400 ppm total copper in the topsoil as a result of many years of Bordeaux mixture spraying of celery. Copper is added to the environment by industrial pollution and vehicular emissions (Shacklette and Connor, 1973), but we have no reports of copper toxicity attributed to these sources. Copper deficiencies in agricultural soils are much more common than copper excesses, and fertilization with copper, especially on highly organic or very sandy soils, is a common practice.

#### Animals --

Under natural dietary conditions

Dick (1956) reported than when sheep graze on pastures of normal copper content, but low in molybdenum (less than 0.1 ppm), copper accumulates in their livers. This accumulation sometimes results in chronic copper poisoning, followed by death. On the other hand, when pasture or forage contains a normal copper content but high molybdenum (5 ppm or more), a poisoning having many of the clinical symptoms of copper deficiency may occur. The average (geometric mean) copper content of United States soils was reported as 18 ppm, with a range of <1-300 ppm, and most soil samples contained <3 ppm molybdenum, with high values ranging from 3-7 ppm (Shacklette and others, 1971).

Under man-induced dietary conditions

Hemkes and Hartmans (1973) found that sheep feeding on either side, and within 20 m of, high-tension copper power lines became ill and died after consuming dry forage and soil with copper in excess of

15 ppm. Sheep appear to be particularly sensitive to copper intoxication. Chronic copper poisoning of animals may occur as a consequence of excessive consumption of copper-containing salt licks or mixtures, or the unwise use of copper-containing drenches. Contamination of feeds with copper compounds from horticultural or industrial sources is a further cause. In all animals the continued ingestion of copper in excess of requirements leads to some accumulation in the tissues, especially in the liver (Underwood, 1971). Copper toxicity in mammals, compared to other animals, is of little significance because they possess barriers to copper absorption. Schroeder and others (1966b, p. 1028) stated, "Avian and mammalian resistance to copper is 100 to 1,000 times greater than is that of more primitive animals." For aquatic organisms copper is the most toxic common heavy metal; this toxicity, however, is inversely related to the water hardness (principally, calcium content). Bowen (1966) reported that a 20 mg Cu<sup>2+</sup> (2,000 ppm) ration in a dry weight diet of 10 g/day was lethal to rats.

#### Man--

Under normal environmental conditions

Underwood (1971, p. 106) stated, "Continuous ingestion of copper from food or water supply at intakes sufficient to induce chronic copper poisoning in man is extremely unlikely, judging by the amounts required for this purpose in other monogastric species." From a normal intake of 2-5 mg/day (Bowen, 1966) there is normally maintained a net balance of zero copper.

Under excessive copper intake

Excessive build-up of copper in the liver and central nervous system, caused by a metabolic inability to excrete copper, is the fundamental cause of Wilson's disease (Scheinberg, 1969). Bowen (1966) reported that 250-500 mg Cu<sup>2+</sup> (330-670 ppm) in a dry weight diet of 750 g/day is toxic to normal individuals. Soluble copper salts, notably copper sulfate, are strong irritants to the skin and mucous membranes (Stecher, 1968).

Fluorine (non-essential for plants; essential trace element for some higher animals, improves animal teeth and bones)

#### Plants--

Under natural conditions

#### Under man-induced conditions

Vegetation in the vicinity of superphosphate plants is often injured by fluorine emissions, and plants growing on soil that has been heavily fertilized with phosphate fertilizers may also receive toxic amounts of fluorine from the soil. However, most toxicity problems have been associated with industrially-polluted air as the major source of fluorine, and this source is indicated by abnormally high fluorine content in the tops of plants, with a corresponding low content in the roots. Depending on species and growth conditions. 30-300 ppm fluorine (dry-weight basis) generally reduces growth (National Research Council, Committee on Biological Effects of Atmospheric Pollutants, 1971). In jury symptoms are leaf-margin necrosis, or interveinal chlorosis, or both. As a result of fluoride emissions from a factory in Czechoslovakia, Marier (1968) reported that within a 5-km distance tree leaves were necrosed, had a decreased chlorophyll content, and contained 7 to 72 times more fluorine than that normally found. Vegetables and fruit were disfigured in shape and color, and contained 5-21 times the fluoride of control samples.

#### Animals ---

Under natural dietary conditions

Animals obtain their fluorine from the plants which they eat and the water which they drink (Brewer, 1966a). The fluorine levels of common uncontaminated feed materials are too low to constitute a fluorine hazard to livestock, but endemic fluorosis has been reported from areas where the drinking water contains unusually high fluorine content (Underwood, 1971). Lethal fluorosis of sheep and other livestock, caused by consuming contaminated vegetation and water, occurred following a volcanic eruption in Iceland (Thorarinsson, 1970).

Under man-induced dietary conditions

Herbage and water supplies of animals that have been contaminated by dust from rock phosphate deposits and mines have caused chronic fluorosis. Whereas surface waters usually contain less than 1 ppm fluorine, water from deep wells in endemic fluorosis areas contains 3-5 ppm fluorine and often 10-15 ppm (Underwood, 1971). Bowen (1966) reported that 0.1 mg F<sup>-</sup> in a 10 g/dav drv weight diet (10 ppm) is toxic to rats, whereas 30 mg (3,000 ppm) is lethal. The following concentrations of fluorine in dietary dry matter above which normal performance may be affected follow: beef or dairy heifers, 40 ppm; horses, 60 ppm; finishing cattle, 100 ppm; broiler chickens, 300 ppm; breeding hens, 400 ppm; and turkeys, 400 ppm (National Research Council, Subcommittee on Fluorosis, 1974).

#### Man--

Under natural environmental conditions

Food is the major source of fluorine to individuals not exposed to industrial contamination or to naturally or artificially fluoridated drinking water. Very few foods contain more than 1-2 ppm fluorine, and most of them contain less than 0.5 ppm (dry-weight basis). The consumption of tea can be an important determinant of total dietary fluorine intake, as fluorine concentrations of 100 ppm in tea leaves

are common, two-thirds of which passes into the infusion, so that one cup of tea can add 0.1-0.2 mg fluorine to the diet. Endemic fluorosis from natural waters from deep wells having 20-50 ppm fluorine have been noted as resulting in mottled teeth and bone deformities (Underwood, 1971). Bowen (1966) listed 0.5 mg F in a 750 g/day dry weight diet (0.7 ppm) as the normal dietary intake. Consumption of 20 mg (27 ppm) was considered toxic and 2,000 mg (2,700 ppm) was lethal.

#### Fluoridated drinking water

Community water supplies commonly are treated with sodium fluoride or fluosilicate to maintain fluoride levels ranging from 0.8 to 1.2 ppm, in order to reduce the incidence of dental caries; at concentrations much above these levels, some tooth mottling may occur (Underwood, 1971).

Iodine (non-essential for plants, essential trace element for animals)

#### Plants--

Under natural conditions

Although iodine is highly toxic to plants, it usually is present in very small amounts in an available form in soils, therefore seldom presents a toxicity problem (Martin, 1966b). The iodine content of land plants varies with the species and the amount in the soil. Shacklette and Cuthbert (1967) reported the following average iodine concentrations (ppm, dry matter) for groups of land plants: fleshy fungi, 6.2; ferns, 5.7; coniferous trees, 3.9; monocotyledons, 5.9; dicotyledonous trees, 2.7; dicotyledonous vegetables (edible parts), 6.9. Iodine in marine brown algae ranged from 55-8,800 ppm.

Under man-induced conditions

Large applications of kelp (marine brown algae) to soil as fertilizer may cause iodine toxicity to sensitive plants (Martin, 1966b). Adding 2.5 ppm potassium iodide to soil has injured crop plants. In nutrient solutions and sand cultures, iodine is toxic to plants at concentrations greater than about 0.5-1 ppm (Martin, 1966b).

## Animals--

Under natural dietary conditions

We have no reports of iodine toxicity in animals fed normal rations. The iodine levels in vegetation in some areas are inadequate for animal requirements, and iodine supplements must be used in the feed. Under man-induced dietary conditions

In experimental studies, significant species differences in tolerance to high intakes of iodide were found, but in all species studied the tolerance was high in comparison with normal dietary iodine intakes, indicating an extremely wide margin of safety for this element. Hens fed 312 to 5,000 ppm potassium iodide in their ration ceased egg production. High levels also increased embryonic mortality in rats and rabbits (Underwood, 1971).

#### Man--

Under natural environmental conditions

Prolonged intake of large amounts of iodine by normal individuals markedly reduces thyroidal iodine uptake—the antithyroidal or goitrogenic effect. In an area in Japan the consumption of large quantities of iodine in the diet was reported as the cause of endemic goiter (Underwood, 1971). However, areas of iodine deficiency, rather than excesses, are by far more common, and iodine supplements to foods are widely used.

#### Iodine tolerances

Bowen (1966) listed 0.2 mg I in a 750 g/day drv weight diet (0.3 ppm) as normal, whereas 10,000 mg (13,300 ppm) was toxic. Thomas (1973) gave 5-50 mg/kg body weight as the probable lethal dose of iodine for an adult.

## Lead (non-essential for plants and animals)

#### Plants--

Under natural conditions

We can find no reports of definite toxicity symptoms in plants that grew in areas of natural enrichment of lead only. Lead, zinc, and other heavy metals often occur together in mineralized outcrops, therefore it is difficult to associate observed toxicity symptoms in plants at these sites with lead alone. These plants may absorb large amounts of lead without exhibiting toxicity symptoms; concentrations in stems of certain shrubs may be as high as 350 ppm lead in ash of the samples (Shacklette, 1960) without producing visible toxicity.

## Under man-induced conditions

Elevated levels of lead in plants affected by automotive and industrial contamination have been extensively reported. However, we have no reports that conclusively demonstrate toxicity to the plant of such contamination. Frank toxicity of lead to plants has been shown. insofar as we are informed, only by very few laboratory and field experiments. Wieler (1938) added lead salts to acid soils and produced injury to oak and birch trees, but not to spruce trees. Prát (1927) studied uptake of lead from lead chloride solutions, and found that broad-beam plants (Vicia faba) absorbed all the lead in less than three days, but grew very little as a result . Hooper (1937) found that French beans (Phaseolus sp.) growing in solution cultures were damaged by 30 ppm of lead as the sulfate alone, or in combination with nutrient salts. Plants spraved with lead sulfate solutions were not injured unless sufficient lead residue was left to block the stomates. Wilkins (1957), using lead nitrate as the nitrogen source, grew sheep fescue (Festuca ovina) in solution cultures and reported that root growth was measurably retarded with 10 ppm of lead, markedly reduced by 30 ppm, and stopped at 100 ppm. Miller and Koeppe (1970) showed that 60 umoles of lead nitrate added to a nutrient solution retarded growth of young corn plants when phosphate was deficient (in young leaves the concentration of lead was 115 ppm in dry weight). At 600 umoles and greater

(concentration of lead in young leaves was 306 ppm, dry weight) marked reduction in growth of corn was noted with or without sufficient phosphate. The use of lead arsenate as an insecticide in orchards for long periods has caused high lead concentrations in these soils. Regarding the toxicity of these soils, most of the observed damage to subsequent plant growth can be attributed to the resulting arsenic concentrations. Connor, Shacklette, and Erdman (1971) found 2 percent lead in ash of a cedar tree (Juniperus virginiana) that had been contaminated by dust from passing ore—carrying trucks; washing the samples with different solvents did not appreciably reduce the lead content. This tree showed no toxicity symptoms. Most of the lead in soils is sparingly soluble and largely unavailable to plants. Brewer (1966b) reviewed the reports of soluble lead in many different soils, and found most of them to contain less than 1 ppm.

#### Animals--

Under natural dietary conditions

McMurtrey and Robinson (1938, p. 821) wrote, "Normally the quantities [of lead] in edible plants or parts thereof are so small as to have no effect on the health of the animal eating the plant." Shacklette (1962) estimated that a large browsing animal eating native tree and shrub foliage in Alaska might ingest from 1 to 4 grams of lead annually, depending on the region of the State.

Under man-induced dietary conditions

Lead from industrial operations and vehicular traffic may be absorbed by, or accumulated on, forage plants to the extent that the plants are toxic to grazing animals. Lead poisoning in cattle and horses that grazed near smelters has been reported in Germany by Hupka (1955), in the United States by Hammond and Aronson (1964), in Ireland by Igan and O'Cuill (1970), and in Canada by Schmitt, Devlin, Larsen, McCausland, and Saville (1971). The latter authors reported that excessive amounts of lead in ingested forage was the primary cause of a chronic debilitating disease of six young horses and less acute, but similar, disorders in 25 older horses. Cattle were less seriously affected. The lead values in the pasture grasses were as follows (ppm, dry-weight basis): spring, 1-46; midsummer, 4-310; fall, 4-435; and overwintered grass, 25-2,800. Animals in the Staten Island 200, ranging from reptiles to primates, suffered acute lead poisoning attributed largely to intake of lead from atmospheric fallout (Bazell, 1971). Schroeder and Balassa (1961b, p. 417) stated. "It [lead] is not as toxic orally for mammals as cadmium and mercury, but is more so than copper, manganese, silver, vanadium, zinc, chromium, molybdenum, cobalt, nickel and probably arsenic." They also reported that 0.01-1.0 ppm lead (chloride) immobilized Daphnia magna and at 0.1-50 ppm was lethal to various fishes. For comparison, they noted that this was the range of toxicity to these organisms for zinc and nickel. Migratory waterfowl have been reported to be poisoned by ingesting lead shot that were lodged in bottom sediments. Many other reports could be cited of poisoning of animals by lead that was introduced into the environment by human activity.

#### Man--

Under natural environmental conditions

Lead poisoning from natural sources is very unlikely. Brewer (1966b, p. 214) commented, "The extremely low lead content of edible parts of the majority of crops is reassuring, in light of the potential toxicity of lead to animals, including man." Schroeder and Balassa (1961b) reported that poisoning of man has occurred when drinking water with 0.18 to more than 1.0 ppm Pb2+ (0.4-2.5 mg daily, in addition to lead in food) has been consumed over an unspecified period of time. Water should not exceed 0.05 ppm lead (World Health Organization, 1963). "Normal" rural air contains about 0.05 ug lead per cubic meter (Patterson, 1965). However, it should be pointed out that very few humans today live in a natural, unpolluted environment.

Lead intakes and toxicities

The average daily intake of lead from food and beverages in the United States is now estimated at about 0.30 mg, with only about 10 percent of this being absorbed from the intestinal tract. In addition, some lead is inhaled and absorbed through the respiratory tract: the relative importance of this respiratory exposure is a matter about which there is some dispute (Goldsmith and Hexter, 1967). These authors concluded that the absorption of lead from the two sources may be of similar magnitude. In another study (Rabinowitz and others, 1973) in which a healthy man was fed a diet normal in lead content and labeled with lead-204 it was concluded that about twothirds of his assimilated lead was dietary in origin and the remainder was inhaled. Studies have generally shown that less than 10 percent of ingested lead is absorbed, whereas 25-50 percent of inhaled lead is absorbed (Goldsmith and mexter, 1967). The possible physiological significance of environmental lead was discussed at length by Warren (1974), who listed the sources of lead insult as air, dust, leaded paint, cigarette tobacco, beer and wine, drinking water, food, fertilizers (particularly, sewage sludge), leaded gasoline, and miscellaneous, which included smelters, vegetables grown over refuse dumps, glazed pottery, plastics, solders, and fillers in alkaline piping. Bowen (1966) reported that the normal consumption of Pb<sup>2+</sup> in a 750 g/day dry weight diet was 0.3-0.4 mg (0.4-0.5 ppm) and that a consumption of 10,000 mg (13,300 ppm) on the same basis may be considered lethal. Schroeder and Balassa (1961b) speculated that poisoning in man would be eventually achieved if 1 or 2 percent of the total bodily content (80 mg) were ingested daily (0.8-1.6 mg). Patterson (1965) noted that a concentration of Pb2+ in the blood of 0.5-0.8 ppm is the threshold for acute lead poisoning.

Lithium (non-essential for higher plants and animals, but an essential trace element for some micro-organisms)

#### Plants--

## Under natural conditions

Naturally-occurring instances of lithium toxicity to plants are not known, except in the case of citrus (Bradford, 1966b), which are very sensitive to small amounts of lithium. However, a report on lithium in the environment (Mertz, 1974b, p. 40) stated, "Crops grown in closed basins in California, Nevada, and Arizona are exposed to toxic levels of lithium." Lithium excesses occur most commonly in soils derived directly from igneous rocks rich in ferromagnesian minerals, and in soils derived from sedimentary deposits rich in clays or micas (Bradford, 1966b). The lithium concentration in 912 samples of soils from throughout the conterminous United States was reported (Shacklette and others, 1973) as follows: range, 5-136 ppm; Bradford (1966b, p. 221) stated, "There is arithmetic mean, 24.7. no evidence available to indicate that total lithium in soils is in any way related to plant availability. - - - Plant content of this element is at present the best guide to the lithium status of the soil."

#### Under man-induced conditions

Many crops are susceptible to injury when lithium is applied to the soil in the form of soluble salts (McMurtrey and Robinson, 1938), and many plants are tolerant of high lithium levels (Mertz, 1974b). Lithium was toxic to citrus when concentrated in soil (as Li2SO4) to 2-5 ppm, and when concentrated in leaves to 140-220 ppm in dry weight (Alcrich and others, 1951). Lithium toxicity has also been observed in avocado, celery, corn, olive, and wheat. In contrast, cotton seems to be completely resistant to lithium toxicity, even up to one ton of lithium nitrate per acre. Lithium content in citrus leaves ranging from 4 to 40 ppm in dry weight has caused moderate to severe toxic effects (Sauchelli, 1969).

#### Animals --

We have no reports of lithium toxicity in animals.

#### Man--

Toxic symptoms that have been reported at the pharmacological dose level in humans include development of goiter and congenital malformations (Mertz, 1974b). Massive doses of lithium were reported to reduce aggressive behavior in humans and other vertebrates (Levv, 1968). Bowen (1966) gave as the toxic dose in humans 200 mg/day Li<sup>+</sup> in a 750 g dry weight diet (270 ppm).

## Magnesium (major essential element for plants and animals)

#### Plants--

Under natural conditions

frue toxicity apparently is unknown. Kelly (1948) cited an example of a soil near Napa, California in which more than 90 percent of the cation exchange capacity was saturated with magnesium, and stated that this soil was almost completely unproductive. In this case, the inhibition of vegetation was due to deprivation of other elements induced by excess magnesium, not to the magnesium itself.

Under man-induced conditions

Sievers (1924) reported that magnesium oxide dust from a magnesite plant in the State of Washington was deposited on the surface of adjacent soil in quantities great enough to be toxic to plants. In sand culture experiments, Carolus (1935) showed that magnesium toxicity in potatoes resulted when magnesium was extremely high and potassium was extremely low.

#### Animals--

Under natural conditions

High levels of available soil potassium reduce magnesium uptake by plants, especially in low magnesium soils, and this condition may produce pastures (especially grasses) that are extremely low in magnesium (<0.2 percent, dry weight basis). Animals grazing on this grass may develop a nutritional disease called hypomagnesaemia or grass tetany (Mortvedt and Cunningham, 1971).

Under man-induced conditions

We have no reports of magnesium toxicity in animals.

#### Man --

We have no reports of magnesium toxicity in humans.

## Manganese (essential trace element for plants and animals)

#### Plants--

Under matural conditions

Morris (1949) found that the exchangeable manganese content of 25 naturally acid soils varied from 1.2 to 638 ppm. Lespedeza and sweet clover grown on these acid soils made poor growth, contained high concentrations of soluble manganese, and showed typical symptoms of manganese toxicity. In general, plants having more than 400 to 500 ppm manganese (dry weight basis) in their tissues showed toxicity symptoms.

Under man-induced conditions

Reuther, Smith, and Specht (1949) found that 600-800 pounds of manganese had accumulated in the top foot (approximately equivalent to 300-400 ppm) of acid sandy soils in Florida after 15 years of continuous fertilization of orange trees with manganese compounds. These amounts were toxic to some plants. Amounts found in comparable virgin soils were 30-40 pounds total manganese per acre (15-20 ppm). Plant species range greatly in their tolerance of excess manganese;

Fergus (1954) found that kidney beans, a good indicator plant for excess manganese, showed toxicity symptoms when grown on a soil of less than pH 5.0 because of the easily reducible manganese in the soil. Schroeder, Balassa, and Tipton (1966) reported the following toxic concentrations (ppm) of the divalent manganous ion in water supplied to cultures: yeast, 550; legumes, 1-10; orange and mandarin seedlings, 5; tomatoes, 5-10; soybeans, 10-25; flax, 25-100; and oats, 150-500.

#### Animals --

Under natural dietary conditions

Cotzias (1962) reported from the literature that spontaneous lactation tetany has been recorded in cows grazing on pastures high in manganese. Further, consumption by animals of large amounts of certain tree foliage, which contains more manganese than do most herbaceous plants (Shacklette and Severson, 1975), potentially could be toxic.

Under man-induced dietary conditions

The Mn<sup>2+</sup> form has a low order of toxicity to living organisms, especially to vertebrate animals (Schroeder, Balassa, and Tipton, 1966). The hexavalent form is highly toxic but does not occur in nature. The above report listed the following as toxic concentrations (ppm) of Mn<sup>2+</sup> in foods: Laphnia magna, 50; flatworms, 700, freshwater fish, 2,420-3,450; birds, 4,800; chicks, 4,800, rats, >2,000; rabbits, 1,250-6,000; pigs, 500-2,000; and lambs, 5,000.

#### Man --

Underwood (1971, p. 202) reported, "Chronic manganese poisoning occurs in miners working with manganese ores. The manganese enters the lungs as oxide dust from the air and also enters the body via the gastrointestinal tract. The disease is characterized by a severe psychiatric disorder (locura manganica) resembling schizonhrenia, followed by a permanently crippling neurological (extrapyramidal) disorder clinically similar to Parkinson's disease." Cotzias (1962) reported that a particle size of manganic oxide <5 $\mu$  was responsible for the disorder. Bowen (1966) reported that the normal consumption of Mn<sup>2+</sup> in a 750 g/day dry weight diet was 3-10 mg (4-12 ppm).

# Mercury (non-essential for plants and animals)

## Plants--

Under natural conditions

Mercury in living tissues is believed to be largely organic and primarily methyl mercury. The conversion of inorpanic mercury to methyl mercury or dimethyl mercury is accomplished by anaerobic bacteria in the bottom muds of streams. Dimethyl mercury, stable in alkaline solutions, dissociates to ionic methyl mercury at low pH values such as may exist in the anaerobic bottom muds of streams and lakes. Methyl mercury is soluble in water, and is available for incorporation into the tissues of aquatic organisms, thus can enter

the food chain of higher animals and man. Or the methyl mercury may enter the higher organisms by direct assimilation from the surrounding medium (Greeson, 1970). Mercury compounds inhibit the growth of bacteria, and have long been used as antiseptics and disinfectants. In contrast, most higher (vascular) plants are remarkably resistant to mercury poisoning, although they may accumulate high concentrations of mercury in their tissues. Shacklette (1970) reported as much as 3,500 parts per billion (ppb) in dry material of Labrador tea that grew where its roots were above cinnabar mineral deposits, but the plant showed no toxicity symptoms. The geometric mean mercury concentration in 912 samples of soil from throughout the conterminous United States was reported as 71 ppb (Shacklette and others, 1971). Shacklette (1970) stated that the few available reports of mercury analysis of plants suggest that this metal is not concentrated to a great extent, if at all, in the tissues of most plants that grow in normal soils. Mosses are tolerant of high mercury levels in their substrate (Shacklette, 1965).

## Under man-induced conditions

Fungicides containing mercury compounds have been widely used on agricultural and horticultural crops. These compounds, if sprayed on plants, may be absorbed by the plants and translocated from one part of the plant to another. Novick (1969) stated that mercury compounds from sprays applied to apple leaves may be translocated to the fruits, and also may be moved from potato leaves to the tubers. In addition, the sprays may produce surficial deposits on the leaves that are not easily removed. The mercury compounds, as applied, have no toxic effects on the plants themselves. Shacklette and Connor (1973) reported 0.5 ppm mercury (dry weight basis) in Spanish moss plants that presumably resulted from airborne industrial pollution, but toxic effects on the plants were not noted. Some greenhouse flowers, notably roses, are sensitive to volatilized elemental mercury, in that very low concentrations in the air cause toxic symptoms (Shacklette, 1970).

## Animals ---

Under natural dietary conditions

We have no reports of toxicity resulting from animals grazing on normal vegetation; it is likely that the small amounts present in the plants are well within the elimination rates of animals. Wershaw (1970, p. 31) stated, "Natural surface waters contain tolerably small concentrations of mercury except in areas draining mercury deposits." Under man-induced dietary conditions

The concentration of mercury in crop plants that was derived from the soil probably is never toxic. However, the mercury compounds applied as fungicides to plant leaves, seeds, and grains may reach levels that are toxic to animals. Bowen (1966) reported that the consumption of 8 mg/day  $\rm Hg^{2+}$  in a total dry weight diet of 10 g (800 ppm) was lethal to rats.

#### Man--

Greeson (1970, p. 33) stated, "Aquatic organisms, as well as man, will concentrate mercury within their bodies - - -. The result - - - is a buildup with time to the extent that the accumulated mercury can become toxic and, eventually, lethal." In Japan about 50 persons out of more than 100 affected died of the "Minamata disease." caused by the consumption of fish and shellfish obtained from a bay that had received large amounts of methyl mercury compounds in the waste effluents from a plastics factory (Kurland and others, 1960). Mercury poisoning among citizens of Iraq who consumed bread made from seed wheat that had been treated with methyl mercury was reported by Bakir and others (1973). They stated that the wheat contained 8 ppm mercury, and acute concentrations (resulting in many patient deaths) were measured at 0.5-0.8 mg Hg/kg body weight. The biological half-life of methyl mercury in man is about 70-80 days. It is readily absorbed by the gastrointestinal tract. Löfroth (1972, p. 66) stated, " - - - clinical methylmercury poisoning in adult people can occur at a mercury level of about 400 ng/g in the red blood cells - - - corresponding to a regular daily intake of 0.3 mg mercury as methylmercury, i.e. 0.004 mg/kg body weight." Bowen (1966) reported that the normal daily consumption of Hg2+ was from 0.005-0.02 mg when based on a 750 g dry weight diet (0.007-0.03 ppm). Consumption of 150-300 mg on the same basis (200-400 ppm) was considered lethal. The U.S. Public Health Service (1961) proposed a tentative upper limit of 5.0 ppb of mercury in drinking water.

# Molybdenum (essential trace element for plants and animals)

## Plants--

Under natural conditions

There are no recorded instances of a field occurrence of molybdenum toxicity to plants (Johnson, 1966), although high levels may be accumulated in the plants. Dye and O'Harra (1959) reported that among forage plants legumes usually collect more molybdenum than do grasses, and cited a high value of 372 ppm molybdenum (dry weight basis) in a sample of black medic (Medicago lupulina) from a Carson Valley, Nevada ranch. Warren and Delavault (1965) stated that many trees and lesser plants growing over commercial, or potentially commercial, molybdenum deposits may be expected to carry upwards of 500 ppm molybdenum in their ashes, and that relatively few should be found with less than 250 ppm. Deficiency levels for plants are usually indicated by less than 0.10 ppm in their tissues (Johnson, 1966).

Under man-induced conditions

Toxicity in the plant is observed only under extreme experimental conditions; in solution culture experiments using 1,000-2,000 ppm molybdenum, tomato plants developed an intense golden yellow color in their leaves, and seedlings of cauliflower turned an intense purple (Johnson, 1966).

## Animals --

Under natural cietary conditions

"Molybdenum toxicity, variously referred to as molybdenosis, teart disease, and peat scours, has been reported from many parts of the world - - -. In most instances toxic amounts of molvhdenum in forage consumed by ruminants have resulted from naturally occurring excess molybdenum in the soil or irrigation water" (Johnson, 1966, p. 287). This toxicity in ruminants is a complex matter, involving not only excess molybdenum but also low copper levels and high sulfate-sulfur concentrations in the forare. Molybdenosis occurs when the copper in forage is normal (8-10 ppm in dry matter) and the molybdenum is above normal (above 5-6 ppm for cattle or 10-12 ppm for sheep) (Dye and O'Harra, 1959). Molybdenosis in grazing animals has been observed in Nevada and Oregon (Kubota and others, 1961 and 1967). The amount of molybdenum absorbed by plants is not strongly correlated with total molybdenum in the soil, because soil pH and other soil properties greatly affect availability to plants, it being more available at high pH values.

## Under man-induced dietary conditions

Applying molybdenum fertilizers, or liming to release previously unavailable molybdenum, may result in the forage containing amounts of the element that are toxic to animals. Mining activities may expose deposits having concentrations of molybdenum and other elements that can be considered anomalous in the natural geochemical environment of plants and animals. An area in Missouri was studied (Ebens and others, 1973) where clay mining operations had contaminated adjacent areas to the extent that beef cattle grazing these areas exhibited symptoms of metabolic imbalance thought to be chronic molybdenosis due principally to copper-molybdenum imbalance. Bowen (1966) reported that 5 mg MoO<sup>+</sup> (molybdate) in a 10 g/day dry weight diet (500 ppm) was toxic and 50 mg (5,000 ppm) was lethal to rats. Due to poor absorption, horses and pigs have low susceptibility to molybdenosis (Underwood, 1971).

#### Man--

At normal environmental concentrations of molybdenum, toxicity is of little concern. Underwood (1971, p. 135) stated, "Molybdenum is apparently of so little practical significance in human nutrition, either in health or disease, that few people have been stimulated to undertake studies with this element." The only incidence of molybdenosis in humans of which we are aware was reported by Aparwal (1975). He found that peasants in India who consumed sorghum as a staple that was grown in alkaline soils high in molybdenum and fluorine developed a crippling syndrome of knock-knees (genu valgum). No instances of the disease were reported prior to the construction of a large dam that raised the water table in the surrounding district and caused an increase in alkalinity and concurrently the uptake of molybdenum by the sorghum. No specific concentrations of molybdenum in sorghum, soils, or humans were given.

## Nickel (non-essential for plants and animals)

#### Plants--

Under natural conditions

Mitchell (1945) stated that the normal nickel content of plant material, dry weight basis, ranges from 0.10 to 5 ppm, depending on the species, the part of the plant, maturity, time of sampling, and other factors. Excessive nickel in serpentine soils may be a contributing factor to the restricted growth of plants on these soils, as reported by many investigators, but excessive chromium, unfavorable magnesium-calcium ratios, and deficiency of molybdenum may also limit plant growth (Vanselow, 1966a). The amount of nickel absorbed by plants on serpentine soils ranges wicely among species; Shacklette (1966) reported the following concentrations (ppm in ash) from a site in Alaska: aspen, 10; white birch, 50; and low juniper, 150. The soil at this site contained 50-75 ppm nickel, and the basaltic greenstone on which the soil developed contained 100 ppm nickel. Malyuga (1964) described apetalous forms of anemone growing over nickel deposits, attributed to toxicity of the nickel.

Under man-induced conditions

Toxicity to many plants, even at relatively low concentrations, has been noted; 40 ppm (dry weight basis) in tomato plants was toxic, and 150 ppm stopped growth (Sauchelli, 1969). Soane and Saunder (1959) reported 12-246 ppm (dry weight basis) in leaves of corn, and 14-34 ppm in leaves of tobacco--both kinds of plants developed toxicity symptoms.

## Animals--

Under natural dietary conditions

Mitchell (1945) recorded levels of 0.5-4 ppm (dry weight basis) nickel in pasture herbage; Allaway (1968) reported that toxicity to animals was moderate to low. In view of these relationships, toxicity to grazing animals seems unlikely.

Under man-induced dietary conditions

Compared to many other trace metals, the concentration of nickel in foods is high. There appears, however, to be a mechanism in mammals limiting its intestinal absorption. The toxicity of nickel to mammals is low (ranking with the essential trace elements) except in astringent doses. Nickel salts irritate the mucosal lining of the gut more than they cause inherent poisoning (Schroeder, Balassa, and Tipton, 1962b) Underwood (1971) reported that 700 ppm nickel in the diet of chicks depressed growth, 1,600 ppm depressed growth of young mice, and 1,000 ppm had no apparent toxic effect on rats or monkeys. Bowen (1966) gave as toxic to rats a ration of 50 mg Ni<sup>2+</sup> in 10 g/d of dry weight diet (5,000 ppm). He listed the element as potentially carcinogenic.

## Man--

The toxicity of nickel to humans is low. workers in nickel refineries have developed "nickel dermatitis" and respiratory-tract neoplasia; a direct link between the elemental form and these pathologies, however, has not been made (Schroeder, Balassa, and Tipton, 1962b).

Selenium (non-essential for plants, essential trace element for animals)

Plants--

Under natural conditions

The occurrence and ecological relationships of selenium-indicating plants has been documented by many investigators. Two groups of native species may be recognized: the primary indicator plants are those found growing only on seleniferous soils and which absorb large amounts of selenium; the second group is composed of those species which are also capable of absorbing selenium in concentrations toxic to animals if growing on seleniferous soils but which may also grow elsewhere. Excess soil selenium may prevent plants not in these two groups from growing on seleniferous soils by causing toxicity symptoms to develop. These symptoms are never seen in crop plants grown on naturally seleniferous soils, but in experimental conditions the symptoms in grasses ordinarily are snow-white chlorosis of the leaves, and pink root tissue; symptoms in other plants varv, but commonly include stunting, yellow chlorosis, and pink leaf veins (Ganje, 1966). Lakin (1972) stated that certain species of Astragalus utilize selenium in an amino acid peculiar to these species, and that they absorb many times as much selenium as do other plants growing in the same soil. These plants convert selenium into forms absorbed by other, non-seleniferous, species through foliage decomposition and oxidation to inorganic salts or soluble organic compounds (Ganje, 1966). The plants, both fresh and dried, often have a strong garlicky odor. Byers and Lakin (1939) analyzed about 300 samples of shales, soils, and plants collected in seleniferous areas of Canada and found the selenium of shales to vary from from 0.3 to 3.0; of soils, from 0.1 to 6 ppm; and of vegetation, from 3 to 4,190 ppm in dry matter. The organic compounds of selenium in soil are derived from partially decayed seleniferous vegetation. Inorganic selenium exists as the element; as ion selenide; as a substitute in sulfide minerals, particularly pyrites; as selenite, particularly basic ferric selenite; and as selenate, particularly calcium selenate. Basic ferric selenite seems to be the most common in soils, while very little is present in the elemental form. Selenate and organic selenium are the forms most available to plants (Ganje, 1966).

Under man-induced conditions

Soils producing seleniferous vegetation have been found only in arid or semiarid regions, at least in the United States, where the mean annual rainfall is less than 20 inches. For crop plants, only the soil content of water-soluble selenium is important, because elemental selenium and selenite are of slight availability to these plants, as was demonstrated by Hurd-Karrer (1934) and others. Corn grown in culture solutions containing 5 ppm of selenite or organic selenium accumulated 200 and 1,000 ppm selenium, respectively. At the 10-ppm level, corn accumulated 300 ppm from the selenite form and more than 1,500 ppm from the organic selenium form (Ganje, 1966). Resistance to selenium toxicity among plant species ranges so widely that a general toxicity level cannot be estimated.

## Animals ---

Under natural dietary conditions

Lakin (1972, p. 49-50) reported, "Acute poisoning of cattle and sheep occurs when herds or bands are being driven from one pasturage to another. Animals, under these conditions, eat forage indiscriminately and many may die overnight. Both seleniferous Astragalus species and alkaloids are probably involved. - - Subacute poisoning, known locally as blind staggers, loco disease, or pushing disease, has been reported in western United States and in South Africa. This is probably another instance of the confusion between selenium toxicity and naturally toxic vegetation. The actual cause of these diseases is in debate. Chronic poisoning is caused by daily ingestion of cereals and grasses containing 5 to 20 ppm selenium. - - - Subchronic poisoning has been reported by Brown and de Wet (1962) in South Africa. They suggest - - - that the moderate selenium content of the diets of these animals has weakened them and made them more susceptible to disease." Byers (1935) suggested L pom (dry weight basis) of selenium in plants as a tolerance limit for animals that consume them, and considered 5 ppm to be potentially dangerous. Water containing 0.5 ppm selenium may also be dangerous (Sanje, 1956).

Under man-induced dietary conditions

Because of the dual role of selenium as a micronutrient and a toxin to animals, the selenium concentrations in feeds can be critical factors in the health of the animals. Underwood (1971, p. 346) stated, "A dietary intake of 0.1 ppm [in dry feeds] provides a satisfactory margin of safety against any dietary variables or environmental stresses likely to be encountered by grazing sheep and cattle." Many factors determine the level of selenium in feeds that are toxic to animals, but amounts of 5 ppm (dry weight basis) or more may generally be considered toxic. Underwood (1971, p. 356) stated, "Signs of chronic poisoning are common in rats and dogs given diets containing 5-10 ppm selenium, and, at 20 ppm, there is complete refusal of food and death in a short time. Young pigs fed seleniferous diets containing 10-15 ppm selenium develop signs of selenosis within 2 to 3 weeks. Diets containing lower levels than these would induce similar effects if fed for a longer period. The minimum toxic levels for grazing stock are more difficult to determine. They probably lie close to 5 ppm selenium. Łaible herbage in seleniferous areas commonly contain 5-20 ppm selenium." Sauchelli (1969) reported that as little as 1 ppm selenium in the soil permitted the growth of wheat, but when the grain containing 8-10 ppm selenium was fed to rats, it retarded growth and killed them after a few weeks. Selenium may be introduced into the environment through the burning of coal, in phosphate fertilizers, and in selenium-containing insecticides, but the latter source has very little application to toxicity problems at present because the use of these insecticides on food plants is prohibited, except in special circumstances.

## Man--

Under dietary conditions in seleniferous regions Lakin (1972, p. 51) wrote, "Soils producing crop plants that are toxic because of selenium are confined to small areas but occur throughout the world. Such soils are confined to semiarid regions or areas of impeded drainage. They contribute no significant hazard to human health and only locally to animal health." The selenium content of certain foods may reach levels that could affect human health. For example, the selenium content of tuna was reported (Kifer and others, 1969) to average 4.63 ppm (dry weight basis), and to range from 3.4 to 6.2. A daily intake of 1 mg selenium in food is probably not harmful to an adult person. Robinson (1936) found that seleniferous wheat may be blended with sufficient selenium-free grain to drop the selenium concentration to the tolerance level. Hadjimarkos (1970) reported that the incidence of dental caries appears to be greater in areas naturally high in selenium. This is particularly true among children who consume small amounts of dietary selenium in addition to the naturally high amounts in the local water. Selenium concentrations of 0.08 ppm in the urine identified those individuals with increased incidence of dental caries. The situation regarding selenium poisoning in man was summarized by Lakin (1972, p. 50) as follows: "Fortunately, the human diet is rarely restricted solely to the products of a highly seleniferous area. Thus, selenium poisoning through the food-plant cycle is rare in the world human population and tends to be restricted to combinations of highly seleniferous areas whose populations depend largely on local agricultural produce." Chronic selenium poisoning in humans was reported to occur in Mexico by Byers (1937) and in Columbia by Ancizar-Sordo (1947) and Leonidas and Hernán (1970).

Under the effects of environmental pollution by selenium
Sauchelli (1969) reported that the maximum amount of selenium in
the whole diet that man can consume without ill effects is believed
to be 3 ppm. Bowen (1966) listed as toxic 5 mg SeIV (selenite) in
a 750 g/day dry weight diet (7 ppm). Pollution-related selenium
intoxication is most commonly associated with industrial exposure
(Cooper, 1967) because selenium compounds are absorbed through the
lungs in dust or fumes, and through the skin. Whether ingested or
inhaled, Cooper (1967, p. 186) stated, " - - - there is marked
variations between and within animal species in their response to
selenium at what may be considered toxic levels."

## Thallium (non-essential for plants and animals)

## Plants--

Under natural conditions

Very few cata are available on the normal concentrations of thallium in vegetation. The following ppm in ash were reported (Shacklette and others, in press) for trees and shrubs of the Rocky Mountain region: subalpine fir needles 2-100, stems 2-70; limber pine needles 2-5, stems 3-5; lodgepole pine needles 2-5, stems 3-7; Engelmann

spruce needles 2-10, stems 15; myrtle blueberry stems and leaves 2-7; phyllodoce stems, 2; and ponderosa pine stems 15. Toxic levels were reported by Zýka (1972) in vegetation of a region in Yugoslavia remarkable for high levels of thallium in the substrate. He found thallium in ash of herbaceous plants to range from 10 ppm in Eryngium to 17,000 ppm in bedstraw (Galium sp.). Toadflax (Linaria sp.) contents ranged from 3,000-3,800 ppm. He also noted zonation of species related to soil concentrations of thallium, which indicated the degree of toxicity of the element to certain plant species. Under man-induced conditions

McMurtrey and Robinson (1938, p. 827) stated, "When artificially applied, it [thallium] is probably taken up by the plant, and as little as 35 ppm in sandy soils has practically prevented the growth of plants." Berg (1925) reported 0.1 mg thallium in 100 g (1 ppm) of spinach and rye samples.

#### Animals ---

Under natural dietary conditions

Zýka (1972, p. 94) reported, regarding the high thallium region of Yugoslavia, "The high thallium contents in the plants explain their toxic effects on cattle." We have no other reports of thallium poisoning resulting from the consumption of vegetation.

Under man-induced dietary conditions

Thallium compounds have been widely used in poisoned bait for rodents and animal predators because of their extremely toxic effects on these animals. When this poisoned bait is scattered on the soil, its effects persist for several years (McMurtrey and Robinson, 1938). Bowen (1966) reported that 7.5 mg Tl<sup>+</sup> in a 10 g/day dry weight diet (750 ppm) was lethal to rats.

## Man--

Thallium compounds are highly toxic to humans. McMurtrey and Robinson (1938, p. 827) wrote, "Thallium compounds have been used as depilatories with disastrous effects." Thomas (1973) gave 5-50 mg/kg body weight as the probable lethal dose of thallium salts for an adult, whereas Bowen (1966) listed 600 mg/day in a 750 g dry weight diet (800 ppm) as lethal.

Tin (non-essential for plants and most animals, but recently found essential for rats)

## Plants--

Under natural conditions

Measurable amounts of tin are but rarely found in native plant species and when found are usually in concentrations of 20-30 ppm in ash (Connor, Shacklette, and others, 1975). Harbaugh (1950) reported 17 ppm tin in ash of oak twigs, and Millman (1957) found 0.36 (dry weight basis) in twigs of birch. Wallihan (1966, p. 476) stated, "Unlike lead, tin is generally a biologically innocuous element, as shown by its use for storing and conducting distilled water and in tin-coated food containers. Plants absorb it only to a very

slight extent - - -." We have no reports of tin toxicity to plants that are substantiated by data, although Brooks (1972, p. 225) stated, "Toxicity to plants, severe."

Under man-induced conditions

Prince (1957a, 1957b) reported 2.94 ppm (dry weight basis) tin in corn grains, Duke (1970) reported 0.10 ppm tin in dry material of avocado, and tin was reported in one sample each (ppm in ash) of carrot root (20 ppm), corn grains (30 ppm), and beet root (20 ppm) (Connor, Shacklette, and others, 1975). We have no other reports of tin in food plants. Forty ppm Sn2+ (stannous ion) solution in sand cultures has been reported as not affecting the growth of sugar beets (Schroeder, Balassa, and Tipton, 1964). Willihan (1966, p. 476) wrote, "There appears to be no substantial evidence that tin is essential or beneficial to plants in any way, and it has not been shown to be detrimental under field conditions."

## Animals--

Under natural dietary conditions

We have no reports of animal toxicity attributed to naturally occurring tin in the environment.

Under man-induced dietary conditions

Schroeder, Balassa, and Tipton (1964) reported from the literature that relatively large doses of tin in the diet of laboratory animals are needed to produce toxicity. For cats and rats 30-50 mg/kg body weight, and for dogs 850-1,000 mg/kg, was toxic. They noted that a diet of 1 g every 6-10 days caused death in rabbits after 1 to 2 months. Further, 1,000 ppm tin in a tank of goldfish was fatal after 1.5 hours; at a concentration of 626 ppm, after 4.5 hours.

#### Man--

Bowen (1966) reported 2,000 mg tin as toxic in a dry weight diet of 750 g/day (2,700 ppm). Schroeder, Balassa, and Tipton (1964) reported from the literature that severe gastrointestinal symptoms in man have resulted from consumption of fruit punch (pH3) that contained 2 g/l tin. Tin-plated containers for canned foods can be a source of large amounts of tin, particularly for foods that are acidic. However, the double-lacquered metal cans currently in use greatly reduce the tin in canned foods.

Vanadium (non-essential for higher plants and most higher animals, although reported to be beneficial for some; essential trace element for some algae and other micro-organisms, and for chicks)

## Plants--

Under natural conditions

Pratt (1966) stated that he had found no reports indicating either deficiency or toxicity of vanadium to plants under field conditions. Some food plants may accumulate high levels of vanadium without exhibiting toxicity symptoms, as is shown by the following data (maximum ppm found in ash): snap bean, 700; cabbage, 50; tomato fruits, 30; and asparagus, 20 (Connor, Shacklette, and others, 1975).

#### Under man-induced conditions

Von Scharrer and Schropp (1935) found vanadium to be toxic to germinating seeds, but even more toxic at later stages of growth. Chiu (1953) reported that 500 ppm of vanadium oxide in culture solutions produced toxicity in rice seedlings, and that 1,000 ppm killed all the seedlings. Cannon (1963) conducted plot experiments in a desert environment by adding sodium vanadate to the soil. After a few weeks time, 840 ppm of vanadium was found in the soil water solution, and no planted species was able to grow in the plots during the first season. By the second year after a winter of leaching, four species were grown and harvested from the plots which contained 140 to 560 ppm vanadium in solution. The toxicity symptoms exhibited by these plants were extreme dwarfing and chlorosis. Pratt (1966b) suggested that vanadium toxicity may be indicated by two or more ppm vanadium (cry weight basis) in the tops of pea or soybean plants. He concluded that concentrations of 0.5 ppm or greater in nutrient solutions are toxic to plants, and that additions of the element to soils have produced toxicity for a variety of crop plants. As soluble vanadium, the following solution concentrations were reported as slightly toxic by Schroeder, Balassa, and Tipton (1963): 10-20 ppm for soybeans, 26 ppm for beets, 40 ppm for barley, 20 ppm for wheat, and 22 ppm for oats.

## Animals--

Under normal dietary conditions

We have no reports of toxicity attributed to vanadium in feedstuffs. Under man-induced dietary conditions

Vanadium is a relatively non-toxic metal to animals. Schroeder, Balassa, and Tipton (1963) reported that 160 ppm in the diet of rats over an unspecified period of time was lethal due to pastrointestinal irritation. Similar values were given by Bowen (1960), who listed as toxic to rats 0.5 mg VV (vanadate) in 10 g/day dry weight diet (50 ppm) and 1.5 mg (150 ppm) as lethal. Underwood (1971) gave the following concentrations and manifestations: >20-25 ppm vanadium in the diet resulted in growth depression in chicks; 25 ppm was toxic to rats whereas 50 ppm caused diarrhea and mortality. He listed the following relative toxicities for five elements to rats when fed 25 ppm diets: arsenic < molybdenum < tellurium < vanadium < selenium.

#### Man--

Vanadium is not a particularly toxic metal to man. Not only is vanadium poorly absorbed by the pastrointestinal tract but it results in minimal irritation to the lungs when inhaled. Curran and Burch (1967, p. 98) stated, "A specific toxicity from naturally occurring vanadium salts or those contacted in industry would seem to be minimal." Schroeder, Balassa, and Tipton (1963) fed patients 4.5 mg/day as the oxytartarovanadate for 16 months with no apparent toxicity. Underwood (1971) reported that experiments with ammonium vanadyl tartrate given orally to 6 subjects for 6-10 weeks produced no toxic effects other than some cramps and diarrhea at the larger dose levels.

## Zinc (essential for plants and animals)

#### Plants--

Under natural conditions

Zinc concentrations of 0.43-10.16 percent in New York peat soils were reported by Staker and Cummings (1942) to be severely toxic to vegetable crops such as spinach, lettuce, and carrots. effects of the several metals that commonly are associated with zinc in areas of natural enrichment cannot be distinguished with certainty by visual inspection, therefore visible toxicity effects are often attributed to the zinc. Ernst (1974, p. 3) wrote (translated): "In nature soils rich in heavy metals are found over ore bodies which crop out at the surface or extend in the near surface zone at least up to 30 meters. - - - Because of the diversity of bedrock types the distribution of the quality and quantity of heavy metals in the naturally metal-rich soil is quite variable. - - -At a concentration of at least 0.1 percent all heavy metals have a strongly selective effect on vegetation. As a rule, zinc-rich soils (0.1-10 percent zinc) are distinguished by also having a high content of lead (0.1-3.2 percent), but not of cadmium." Many reports in the literature of zinc toxicity to veretation in natural environments are based on circumstantial evidence, in that the exact cause of the symptoms was not determined.

Under man-induced conditions

Contamination of vegetation with zinc, as well as with other heavy metals, is common in the vicinity of metal-working industries. For example, Ernst (1974) reported the concentrations in soil (mg/kg, dry soil) with distance from the sources as follows: zinc smelter, at 250 m, 4,500; at 400 m, 1,300; and at 4,000 m, 210. Brass foundry, at 250 m, 4,520; at 400 m, 350; at 4,000 m, 173, and at 10,000 m, 91. These zinc values contrast with the geometric mean zinc concentration in United States soils of 44 ppm (Shacklette and others, 1971). Thorne, Laws, and Wallace (1942) found that total zinc differentiated zinc-deficient soils from those not deficient in zinc as well as did Hibbard's extraction procedure, but researchers prefer to judge deficiencies and toxicities on the basis of soluble zinc in soils. The zinc content of plant leaves as indicative of nutritional sufficiency and toxic excesses was summarized by Chapman (1966) as follows: deficiency levels are characterized by less than 20-25 ppm in dry matter; ample but not excessive levels, 25 to 150 ppm; amounts greater than 400 ppm may indicate zinc excess. However, there is a wide range in content of zinc among plant species; likewise, tolerance to high levels of soil zinc ranges widely. For example, Robinson, Lakin, and Reichen (1947) reported that a good indication of zinc mineral outcrops is the presence of luxuriantly growing ragweed when other vegetation is stunted. At the location that they studied, total zinc in the soil was 12.5 percent.

## Animals --

Under normal dietary conditions

We have no reports of zinc toxicity to animals resulting from the consumption of ordinary feedstuffs. Underwood (1971, p. 242-243) stated, "Zinc is relatively nontoxic to birds and mammals and a wide margin of safety exists between normal intakes and those likely to produce deleterious effects. Rats, pigs, poultry, sheep, and cattle exhibit considerable tolerance to high intakes of zinc, the extent of the tolerance depending upon the composition of the basal diet, particularly its content of minerals known to affect zinc absorption and utilization, such as copper, iron, and cadmium."
Under man-induced dietary conditions

Zinc compounds are relatively non-toxic to organisms, particularly to mammals. Schroeder and others (1967) reported that a diet for laboratory animals with 0.25 percent (2,500 ppm) zinc salts is apparently non-toxic. The following summary was obtained from Underwood (1971): rats with dietary intake of 2,500 ppm zinc, no discernible effects; 5,000 ppm, severe growth depression, severe anemia; and 10,000 ppm heavy mortality. Weanling pigs with dietary intake of 1,000 ppm zinc, no ill-effects; higher levels, growth depression; and 4,000-8,000, high mortality. Lambs with dietary levels of 1,000 to 1,500 ppm zinc, depressed feed consumption, reduced gains, increased mineral consumption. Steers with dietary levels of zinc of 500 ppm or less, no detrimental effects; 900 ppm, reduced gains and lower feed efficiency; and 1,700 opm caused, in addition, a depraved appetite with excessive salt and mineral consumption and wood chewing. Bowen (1956) listed 50 mg Zn<sup>2+</sup> in a 10 g/day dry weight diet (5,000 ppm) as toxic to rats and 150 mg (15.000 ppm) as lethal.

#### Man\_\_

Unlike the aberrant syndromes for most of the essential trace elements, there has been no primary disorder of zinc metabolism described for humans. Underwood (1971) noted that there existed a wide margin of safety between normal zinc intakes and those likely to produce deleterious effects. Acute zinc poisoning is commonly reported, however, when acidic foods stored in galvanized iron containers have been ingested. Schroeder and others (1967) speculated that cadmium intoxication may also be associated with these cases. Thomas (1973) listed as probably lethal to adults 50-500 mg/kg body weight of zinc salts (chloride, sulfate, acetate, and others).

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# APPENDIX V.

# CHEMICAL ELEMENTS IN VEGETATION AND SOIL NEAR COAL-FIRED POWERPLANTS, WESTERN ENERGY REGIONS

		Pa	age
Table	1.	Surface and subsurface soil, and sagebrush east of Dave Johnston Powerplant, Wyoming	1
	2.	Lichen east and west of Dave Johnston Powerplant, Wyoming	8
	3.	Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming 1	11
	4.	Soil and grass southeast of Four Corners Powerplant, New Mexico	31

THE DATA FROM WHICH THIS RETRIEVAL WAS MADE CONSTITUTE A MISCELLANEOUS COLLECTION OF ANALYSES FROM A VARIETY OF FIELD AND THE U. S. GEOLOGICAL SURVEY MAKES NO GUARANTEE OF THE ACCURACY OR COMPLETENESS OF THESE DATA. LABORATORY INVESTIGATIONS.

THE GEOCHEMICAL DATA ARE LISTED BY THE STANDARD SYMBOLS FOR THE CHEMICAL ELEMENT OR COMPOUND IN PERCENT (1) OR IN PARTS PER MILLION (PPM). PROPERTIES NOT CHEMICAL IN NATURE ARE GIVEN IN CONVENTIONAL UNITS. PROPERTIES WHICH MAY APPEAR IN THIS LISTING, BUT WHICH ARE NOT READILY INTERPRETED ARE DEFINED HERE:

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	- TOTAL NITROGEN	- ORGANIC NITROGEN	■ TOTAL PHOSPHORUS	- WATER SOLUBLE SALTS	- POWDER DENSITY (GRAMS PER CUBIC CENTIMETER)	- BULK DENSITY (GRAMS PER CUBIC CENTIMETER)	- SPECIFIC GRAVITY	- LOSS ON IGNITION	- ACID INSOLUBLE	- OIL BY FISCHER ASSAY	- SPENT SHALE BY FISCHER ASSAY	- GAS PLUS LOSS BY FISCHER ASSAY	- OIL, GALLONS PER TON BY FISCHER ASSAY	- H2O, GALLONS PER TON BY FISCHER ASSAT	- SPECIFIC GRAVITY OF OIL	A STREET, C. STREET, S
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DOXY = DISSOLVED OXYGEN

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N = CONSITTUENT NOT DETECTED AT LOWER LIMIT OF DETERMINATION

- CANSTITUTE HOT DETERMINED BECAUSE OF INTERFERENCE CONSTITUTENT LESS THAN GIVEN VALUE, OR IF GIVEN VALUE IS ZERO, CONSTITUENT LESS THAN LOWER LIMIT OF DETERMINATION CONSTITUENT GREATER THAN GIVEN VALUE, OR IF GIVEN VALUE IS ZERO, CONSTITUENT GREATER THAN UPPER LIMIT OF DETERMINATION
  - - I CONSTITUENT PRESENT IN TRACE AMOUNTS B - BLANK, NO DATA AVAILABLE

IF ALL DATA FOR A SAMPLE ARE QUALIFIED BY THE SYMBOL B, IT MEANS THAT THE SAMPLE HAS BEEN SUBMITTED BUT NOT YET ANALYZED. VERY LIKELY, MICH OF THE DATA IN THIS LISTING WILL CONSIST OF A NUMBER IN THE ASCENDING SERIES 0.0001, 0.00015, 0.0002, 0.0003, 0.0005, 0.0007, 0.0015, 0.0020, ..., 0.1, 0.15, 0.2, 0.3, 0.5, 0.7, 1.0, 1.5, 2.0, 3.0, 5.0, 7.0, 10.0, 15.0, 20,0, ..., 10,000, 15,000, 20,000, 70,000, 70,000, AND 100,000. THESE NUMBERS REPRESENT APPROXIMATE MIDPOINTS OF GEOMETRIC CLASSES DEVISED FOR A SEMI-QUANTITATIVE SCHEME OF SPECTROGRAPHIC ANALYSIS DESCRIBED IN U.S. GEOLOGICAL SURVEY BULLETIN 1084-T (MYERS, HAVENS AND DUNTON, 1961). THE ANALYTICAL PRECISION MAY VARY FROM CONSTITUENT TO CONSTITUENT. RECARDLESS OF THE APPARENT NUMBER OF SIGNIFICANT DIGITS CIVEN, ALL DATA SHOULD BE ROUNDED TO ONE OR TWO SIGNIFICANT DIGITS, AND NEVER MORE THAN THREE.

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APPENDIX V.

CHEMICAL ELEMENTS IN VEGETATION AND SOIL NEAR COAL-FIRED POWERPLANTS, WESTERN ENERGY REGIONS

Table 1. -- Surface and subsurface soil, and sagebrush east of Dave Johnston Powerplant, Wyoming

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APPENDIX V. (continued)

Table 1.--Surface and subsurface soil, and sagebrush east of Dave Johnston Fowerplant, Wyoming (continued)

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Table 1. -- Surface and subsurface soil, and sagebrush east of Dave Johnston Powerplant, Wyoming (continued)

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APPENDIX V. (continued)

Table 1. -- Surface and subsurface soil, and sagebrush east of Dave Johnston Powerplant, Wyoming (continued)

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APPE DIX V. (continued)

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and sagebrush	AL 8-S	SA	•	•	•		•					•	0 0 m m	CU PPM-S	SAC		0	n u	<b>1</b> C	-	0	NO.	เก	20	0 0	n u	ò	100	NI PPM-S	SAG	20	10	50	0 4		2	S !	£.	0 0	2 0	0 -	13	
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and	SAMPLE		3G1 A	4 C C C	3625	3634	5 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	出すりの	36540	3654	3059	400	A 3 G 6 B P	SAMPLE		4 5 5	ייייייייייייייייייייייייייייייייייייי	425	3625	3638	3638	364A	145M	4 C C	7 0 0 0 0 X	300	3662	3658	SAMPLE		Kaglap	9	3 6	3	5	200	בי בי בי	9 5	365aP	308	ပ္ထိ	3 2 8	
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APPENDIX V. (continued)

Table 1 .-- Surface and subsurface soil, and sagebrush east of Dave Johnston Powerplant, Wyoming (continued)

	ZR PPM-S		70	70	70	100	100	70	70	70	30	30	70	9 m	70	100
(continued)	ZN/A PPM		540	200	550	530	320	400	270	410	540	480	380	420	300	280
	YB PPM=S	STON	2 1	1	2 L	2 T	8	2 L	2 L	7	2	7 7	2 1	77	2	2 E
IIS COIL FOWER PAR	X bbws	F DAVE JOHNSTON	70 T	20 L	20 L	30	20	20 1	20 L	20 L	20 L	70 T	20 L	30 L	20 1	20 L
BL OI Dave John	V PP™	SAGEBRUSH EAST OF DAVE	100	70	100	150	100	70	70	70	O M	30	70	30	70	5.0
id sageorusii ea	U/A PPM	SAGE	1.6	1.6	1,6	3.0	2.0	1.2	1,2	1.6	e <b>0</b>	8 0	1,6	0.4	1.2	1.2
STITES SOTT	TI & S		0,20	0.15	0,20	0,30	0.20	0,15	0,15	0.15	0.07	0.07	0,20	0,07	0.10	0,15
isore i <u>Sultace and Bubsultace Boll, and Bakedrush east of Dave Johnston FowerPlant, Wyoming</u>	SAMPLE		K3G1AP	K3G13P	K3G2AP	K3G28P	Kagaap	K3G3FP	KJG4AP	Kagaep	Kagsap	KJGSAPX	K3GSBP	k3654P	Kageapx	K3G6ëP
- T 2TORT	LAB. NO.		416136	416187	416135	416132	416156	416125	416130	416172	416202	416142	416140	416145	416131	415179

APPENDIX V. CHEMICAL ELEMENTS IN VEGETATION AND SOIL NEAR COAL-FIRED POWERFLANTS, WESTERN ENERGY REGIONS (continued)

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hnston Powerplant,	LONGITUD D	LICHEN		05 44 404		2 6 6 7	5 43 25	5 40 15	05 40 15	05 34 34	05 34 34	05 21 5	05 21 5	04 59 0(	04 59 0(	-		1	05 47 50	05 47 50	05 49 18	105 49 184	06 10 26	06 10 26		AG PPM-S		,	4		) c		٠ ح	200	۰ د	•	•	•	. ur		•	מות	٠	ĸ.			•	.0	
west of Dave Johns	LATITUDE			50 14N	50 14N 1	2 50 25N 1	2 50 27N 1	2 50 00N 1	2 50 00N 1	2 50 21N 1	50 21N	N9 8 9 0	2 40 36N	2 50 00N	42 50 00N 1				2 SO 15N	2 50 15N	2 50 15N	2 50 15N	2 50 40N	Z O		ASH *				~•.		•	₽,	. ·	٠,		ζ,	٠.	٠,		•			•		'n.		14.7	•
Lichen east and	SAMPLE			0250	OZEO	0450	0450	OREO	OBEO		36		2226	7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	0164812				10281	10261	104K3	1042	13251	DJ32#18		SAMPLE				OZEO	OZEO	0450	0450	0950	0880	116EC	115EC	132EC	<b>332E</b> 1	DJ64E11	364E			102#1	102∺1	304#1	30441	0332417	1 4 7 5 7
Table 2	LAB. NO.	•		192	9	19	9					6	, -	2.0	276/10				20	1 6		7 6	44	417938	8	2	:			792	193	792	192	797	192	19	79.	13	179	41792:	179			, 00,		1793	1753	417929	1793

APPENDIX V. (continued)

Table 2.--<u>Lichen east and west of Dave Johnston Powerplant, Wyoming</u> (continued)
ab. No. SAMPLE CU PPM-S FE %-S GA PPM-S K/A %

NI PPK		9.5														1.5					Y PPR.		20	50	70	70	70	10	70	70	0	70	0.	20		0 (					
NA/A		0.030	0.0	6	0	ò	60	2	.05	0.5	.05	0		0.5	ŝ	090.0	0.	90.	90.		V PPK•S		0	0	ပ	100	0	0	0	0	0	0	0	vo.		100	Э,	0 0	<b>&gt; •</b>	n	2
の またはな パギ		150	0	0	0	0	0	0	0	0	0	0		0	0	300	0	0	0		U/A PPM		-		•	4	•	•	•	•	•	•	•	•		9 8	•	•	•	•	•
₩G %eS		00	• •	•	•	•		•	•	•		•		•	•	0.1	•		•		TI S.S		-:	7	:	0,15	~	٦,	٦.	٦.	∹	~	7	~		0.20	•	٠.	•	7.	-
LI/A PPM	Z	, <b>so</b> ç		· œ	œ	œ	oo.	œ	œ.	œ	œ	80	NO			12		9			S-MGG RS	z	0	0	0	300	0	0	0	0	0	0	0	0	NO	500	0	0	9	9	>
K/A &	DAVE JOHNSTON	Ø 3	•	• •									DAVE JOHNSTO	•		1.4	•	•	•		SI/3 PPM	DAVE JCHNSTO	400	003	3000	101000	1400	2000	100	000	200	8000		146000	DAVE JOHNSTO	126000	010	002	0078	9 0	000
GA PPM.S	CHEN EAST OF	50 M	2 6	50	1.5	70	1.5	** S	10	1.5	25.	20	HEN WEST OF			15					S-Mdd DS	HEN EAST OF	v			~	0 1	iv)	~	10	7	0.1	10	_	HEN WEST OF	10					•
FE # 5	CIG	70°	•	• •	•	•	•	•	•			•	LIC	•		2,0	•	•	•		Samed ed	LIC	10	70		00;	N)	0	5	S	0	0	0	0	רום	150	Ö	Ś	n i	v v	n
CU PPM.S		30												70	50	10	20	<b>S</b>	70		P/A PPM	٠	20	2	0	9009	C	ç	200	ç	00	0	ç	8		6000	0	00	ပ (၁	0	8
SAMPLE		0302801	10450	30460	JORTO	JOREO	316E0	316E0	332E0	332E1	JACEL	364E1		2	30241	30481	30481	33241	332W1		SAMPLE		102501	30250	10450	DJ04E04	JOSEO	30850	J16E0	31660	J32F0	<b>J32E1</b>	364E1	<b>J64E1</b>		D302#13	70541	3042	3000	J32×1	1 4 2 5 0
LAB. NO.		417926	192	1792	1792	1792	1793	1792	1793	1792	1792	1793		1793	1793	19	1793	1792	1793	9	LAB. NO.		1792	1793	1792	417923	1792	1792	1793	:792	1793	1752	1792	1793		417930	1793	1793	1793	1792	1193

APPENDIX V. (continued)

Table 2. -- Lichen east and west of Dave Johnston Powerplant, Wyoming (continued)

LAB. NO.	SAMPLE	YR PPM=S	ZN/A PPH	S-Mdd HZ	ಶ
			J	LICHEN EAST	OF DAVE JOHNSTON
417926	0302E01	vo	140	70	
417931	DJ02502	v	140	100	
417924	DJ04F03	7	160	70	
417923	0304504	ĸ	160	100	
417921	0308605	7	180	100	
417925	DJGREOE	^	180	70	
4:1937	0316607	v	460	70	
417927	0316508	1	520	20	
417933	0332509	кO	220	7	
417929	DJ32E10	ĸ	240	100	
417922	DJ64E11	^	300	200	
411936	DJ64E12	7	280	200	
			J	LICHEN WEST	OF DAVE JOHNSTON
417930	DJ02413	vo	200	70	
417535	DJ62414	ĸ	200	7.0	
417932	DJ04#15	7	200	100	
417934	DJ04#16	7	200	,	
417926	C332417	7	220	150	
417932	DJ32#18	7	260	100	

APPENDIX V. CHEMICAL ELEMENTS IN VECETATION AND SOIL NEAR COAL-FIRED POWERFLANTS, WESTERN ENERGY RECIONS (continued)

ű CRBNT

H d d

4400004444 88000008888 1328

(E) PPR 5000 5000 5000 5000 7000 7000 BA Y Y X 0000000000 # 22. # 22. # 22. 7. 23.2 7. 2 ERIDGER JIM BRIDGER and sagebrush at Jim Bridger Powerplant, Wyoming X T T دے ä ë SOIL NORTH EAST SOIL SURFACE SURFACE LONGITUD 444444 M NC O subsurface soil, LATITUDE 4444441100 440000 CC 00 4444400mmmm Table 3. -- Surface and SAUPLE KABELLIBON 11

•	m n n n	333 70000	22 	11 100000 100000	4W 4000
•	2 2 2 2 2 0 0 0 0	2 2 2 1 0 n 0 0 0 0 n 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	⊒ ⊒ ZZ 0 m 0 m 0 0	
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	9 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0 0 0 0 0 M N IN M	0000 m5 7m	3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	r r 90000 30000
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APPENDIX V. (continued)

Table 3. -- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued)

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APPENDIX V. (continued)

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APPENDIX V. (continued)

Table 3. -- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued)

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APPENDIX V. (continued)

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APPENDIX V. (continued)

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APPENDIX V. (continued)

Table 3. -- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued)

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SAYPLE	384148	BBAIRS	344245	3542468	54836E	いずのしての	W 1 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	かばせていか	カル はいこの かいこう	0 4 5 3 4 5 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	30.7.4	K38*6AS2	38×69S	SAMPLE		38K1AS	187188	3011118	34.745	55.446	シャンション	ひょうこしゅいん	いれがいない	ピュヤンゴモ	34446	K3245A5Z K3545b5Z		ZHEIAS	30F. LES	Karetas2	グインとこの	375239	3rE445	355445	35545	ひないのないといるのではない。		248346
LAB. NO.	164966	6495	6434	6498	6 4 9 7		5472	***	5475	6 4 4 4 5 4 5 4 5 4 5 4 5 4 5 6 5 6 5 6	0 10 10 10 10 10 10 10 10 10 10 10 10 10	16491	6490	LAB. NO.		6495	£ 483	6 4 5 B	O (	1 F 4 7 5	5 4 9 2	707	100	100 100 100 100 100 100 100 100 100 100	6435	164949		6490	6498	154941	0440	6497	9.0	6495	S S S S S S S S S S S S S S S S S S S	5477	•	190

APPENDIX V. (continued)

Table 3 .-- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoning (continued)

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4	34524S	•		•	.67	•	٦.		20	~	٠.	
*	3RS2HS				55	•	Ξ.		20	7	٩.	_
3	3HS3AS		•	•	.40	•	٦,	7	20	~	0	
4	3453HS	-			49	_		^	30	^	ಿ	
3	<b>388448</b>	•	•		.65	•		^	90	1.5	~	
4	3AS4AS	-	•	•	.58	•	∹	_	<b>S</b>	30	٥.	_
~	3854BS	•		•	45	•		^	20	0.6	٥.	
3	3ASSAS	•			96			· <b>1</b> 0	0	_		
9	3855R6	8.0		0.7	<u>.</u>				80	20	0,05	
			iansens	APP 8011.	MIC 30 TS34	RATOCER				,		
164965	K3B41AS2	<b>†</b> 0	•••	6.0	0,483		0,11	<b>.</b>	22	w	0.041	_
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APPENDIX V. (continued)

Table 3 .- - Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued) PPM K & K20 & LA PPM SUBSURFACE SOIL EAST OF JIM PRIDGER 2001111000 200111000 200111000 20011000 200110 GA PPM 2255000550 [e] SAUPLE LAB. NO. 

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Š TOTAL E 2 C COORDED DOCESSOCO 000 1 100 P205 subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued) P X OF JIM BRIDGER Ħ BRIDGER ARIDGER 7777z eessa saaeee MID PPX TEEFZZZJJS 000000000000 50000000000000000 00000000000 ö 0F SUBSURFACE SOIL NORTH SOIL EAST SDUTH asa aa aasa s NB PPM **777 777 77** 5500000000000000 SOIL 000000000000 SUBSURFACE SUBSURFACE NA20 errorers e TANTURES RE CECEESE EZZ 0 110 0 0 0 0 0 0 0 0 0 0000000000 Table 3. -- Surface and SAMPLE LAB. NO. 

APPENDIX V. (continued)

Table 3. -- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued)

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APPENDIX V. (continued)

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APPENDIX	V. CHEMICAL	ELEMENTS IN	VECET	ETATION	AND	SOLL	NEAR COAL-FIRED		Pomerplants,	WESTERN	N ENERGY	reg ion	w	(continued)			
Table 3.	Surface and	subsurface so	듸	and	sagebrush	rush at	Jim Bridger	Powerplant,		Wyoming	(continued)	Ç pe					
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TABLE V. (continued)

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Table 3Surface and nubsurface toll, and seathfulth Et Jim Fidder Powerplant, Woosing (continued)	OTAL S		ณ์ ผ. เม	000000000000000000000000000000000000000	0000000
Table 3.—Surface and subsurface soil, and sacebrush at 11m Bridger Powerplant, Wooming 12.5	۵. د	00000000000	4 PP		
Table 3.—Surface and subsurface acil, and sasebrush at Jim Bridger Powerplant, AS PEH SACEBRUSH WEST OF JIM BRIDGIN 41 44 20% 10 6 50 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		000000000000000000000000000000000000000	CA/A R		
Table 3.—Surface and subsurface soil, and sagebrush et Jim Bridger  LFF. KG. SAWPLE LATITUDE LUNGITUD DIST KH  SAGEBRUSH WEST OF JI  4144 20K 10F 47 554 2  41624		ENTIDOLIS (1000)	CA % JIM BRIDG	7 7 7 7 7 7 7 10 7 7 7 10 10	.81.01.11
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APPENDIX V. (continued)

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ed)	CD/A PPH		4		•	•	•	•	•		•			•	•	•	•	• •		•	•	. · ·			K/A		24	4 4	26	61	30	2.4	58.	58	N 0	
Wyoming (continued)	CA/A &	œ	11,0			•	•		•	; ;	•			æ	•	6		5:	6	•	•	e c			## **	œ		0 0	0	0	0	9 0	0	0	00	
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Jim Bridger	ва РРМ	RUSH SOUTH OF	800	0	0	0	0	⊂ u	n c	. 0	70	100		0	ŝ	n w	n c	0	0	30	0	000	0	•	<b>49</b> (14) (18)	RUSH NORTH O	•	•		•	•		. S . O	•	00	
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APPENDIX V. (continued)

Table 3	Table 3 Surface and subs	subsurface soil, and	nd sagebrush at	Jim Bridger	Powerplant, Wyoming	(continued)	(pa			
Las. NO.	374,78	CH PPM	CU PPM	es Sul Su	GA PPM	¥¢	K/A	LA PPH	LI/A PPM	U E
			SAGEB	BRUSH EAST O	F JIM BRIDGER					
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APPENDIX V. (continued)

Table 3	Table 3 Surface and sub	subsurface soil,	and sagebrush	at Jim Bridger	Powerplant, Wyoming	ing (continued)				
LAB. NO.	SAMPLE	HAG NW	MO PPM	NA/A &	NGG EN	Edd IX	<b>#</b>	P/A PPM	Mdd 8d	SC PPH
			SAGE	BRUSH NORTH C	OF JIH BRIDGER					
416223	ď	•	7	20		¥			,	
1624	35.4	0	7	1		. ·	•	400	08	0
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6.74	  	0 0	0 I	Ξ	0	0	•	400	9 6	
620	) (I	<b>-</b>	~ !	5.5	0	0		800	) v	
623		00	51	.21	0	10 L		909	0 6	<b>&gt;</b> c
1623	7.7.7.5		9 1	. 25	0	0		400	0 6	
1622	3F45	, ,		97	0	0		000	0.6	
1623	34.5	000	. 01	0.340	1 z	33		36000 36000	000	200
			SAGE	EBRUSH EAST O	F JIM BRIDGER				}	•
6633	ā		•							
416251	Kafira Apx	000	- 1	0,145	Z 0	15	•	800	30	-
1622		000	- 1	9:	0	15		900	9 6	•
1625	i.	000	- 4			20	•	800	90	
1 625	15	9 0	n c		0	50	•	600	100	0
1621	F	300	-		٠,	د مد سا	•	9	20	3
41622	7.	000				Ω	•	800	50	
1624	34	30	10	•	<b>z</b> ;		•	00	30	
1623	T.	1000		• •		٠,	•	0	7.0	0
1621	4.0	S		• c	٠,	2 :	•	600	20	0
1621	3.18	100	10	27		<u> </u>		00	50	
l e 2 1	ir.	100	1.5	18	, ,	2 -	•	9 6	0	0
6 2 3	(4 ) (4 )	300	7	_ ~		2 ¥		000	70	0
770	12) L	200	10	12	0		•	) C	0 0	0
7 7 7		700		80		10 1	•		- <b>.</b>	
C 7 c 1	ر با	300		9				36000	0 0 0 m	7 L
			SAGEB	RUSH SCUTH O	F JIM ERIDGER					
1624	3ES14	300	5							
1625	3FS1B	300	2 -	-:		S.	•	400	70	
1522	35.524	500	- 0	n a		S 0	•	о В	20	0
1623	3F52A	200	-	•		2 0	•	9	70	
1622	3557	300			٠,	> ¥		90	70	0
416234	K34834P	300	12	0,115	3 2	n ur	~ 6	24000	70	г Э
* * * *	というこの	300		12	o	0.0	•	7	001	
, n	440000000000000000000000000000000000000	000	<b>~</b> 1	.12	0	15		200	<b>~</b>	0 0
6.00	2000	007	<b>-</b> 1	Ĉ.	0	50		400	ي رو د	
	100	007	_	õ	0	15		, 4	) (	<b>.</b>
7701	9000	100	o <b>.</b>	21	9	15		200	o c	
										•

APPENDIX V. (continued)

Table 3. -- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming (continued)

## U/A PPH K			SAGEBRI	WEST OF	BRINGE					
Security										
10. SAVELE SIAM NORTH OF LINE STATES AND STA		•	•	;						•
1	ば	<b>o</b>	7	. 32	>		•	3		٠ د
1	X ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) (	0	7	17	0		•	000		,
	35:24	ت	15	£.			•	9		
	30,24	C	7	. 19			•	909		
10   10   10   10   10   10   10   10	35.57	C	0	.17			•	900		
	36438	C.	01	10	c		•	400		0
No.	3F + 4 A	C	15	25	0		•	800		0
3	3:144 H	に	0	13	0			800		0
Name	3F.5A	c	,	34	0			200		0
Name	35.458	၁	7	. 56	0			200		0
Name	3446	c		.45	c			400		0
**************************************	37.160	C,		25	0		•	400		0
SACPLE   SI/A PPH   SK PPH   TI 4   U/A PPH   Y PPH	3505	5-		.26	0		•	400		0
23 KASALIAP 120000 0 N 200 0.15 1.2 50 20 L 2 L 0 0 1 1 1 1 1 2 S C C C C C C C C C C C C C C C C C C	AKPL	I/A PP	A A	a. a.	<b>H</b>	/A PP	a.	d.	9	Ω. Ω.
### ### ### ### ### ### ### ### ### ##			AGE	RUSH NORTH	F JIM BRIDG	œ				
## Kähijapx 120000	41756	2000		0	-			_		
10000	94440	000				•		, ,		
### 17207   17	4.5			کا ت	-			3 0	-	
######################################	407.66	7200		3 0	•	•				
### ### ### ### #### #################	でいれる	000		· C		•		, .		
	3823A	7200		0	•					
### ### ### ### #### #### #### ###### ####	38%30	6000		0	-	•				
### ### ### ### ### ### ### ### ### ##	***	7400		0						
A STATE   A STOOM   A ST	3844E	400		0	9			0		
### Kärnsap 56000 O N 500 C.07 O.8 20 L 20	32158	200		0	٠,	•		0		0
NAMERRY   SAGEBRUSH   EAST OF JIN BRIDGER   SAGEBRUSH   SAGEBR	367588	8 0 0		0	0			0		0
Nate late   Nate	3HYSEP	00+		ပ	3	•		0		
Name			AG	BRUSH EAST	F JIM BRIDG	œ				
Name   April	34E14	900	_	O	0	-	15	0		
S         Marking         80000         0 <th< td=""><td>3FE1A</td><td>004</td><td>_</td><td>0</td><td>-</td><td></td><td>30</td><td>ာ</td><td></td><td></td></th<>	3FE1A	004	_	0	-		30	ာ		
2 N3FELEPX 80000 30 SCO 0.15 0.8 30 20 L 0 N 2	BEFIR	9 0 0	-	0	0	•	30	0		
3         N 3 5 5 2 AP         45000         0 N         500         0,07         0,08         15         20 L         0 N           7         N 3 5 5 2 0 0         0 N         200         0,07         0,04         15         20 L         0 N           8         N 3 5 5 2 0 0         0 N         300         0,10         0,4         15         0 N         0 N           1         N 3 5 5 2 0 0         0 N         200         0,20         0,20         0 N	36618	000	0	O	7		30	0		
7         Name         Value         Valu	3= F.2A	500		0	9	•	15	0		
2         K3.57.72 K3.57.74 K3.000 O N         200         0.03         0.4         15 L O N         700           9         K3.57.34 P         150000 O N         300         0.10         0.8         20 L O N         0 N           1         K3.57.34 P         200000 O N         150         0.20         0.8         20 L O D         0           3         K3.67.44 AP         180000 O N         150         0.20         1.2         0         0           3         K3.67.44 AP         120000 O N         150         0.20         1.2         0	38528	00%		0	٥.		15	0		
9         K3FE3AP         52000         0.0         300         0.10         0.4         15         20 L         0.N           1         K3E5AAP         200000         0.N         200         0.20         1.2         0.0 <t< td=""><td>3 1 1.2 5</td><td>200</td><td></td><td>0</td><td>0</td><td></td><td>'n</td><td>0</td><td></td><td>00</td></t<>	3 1 1.2 5	200		0	0		'n	0		00
1         K3+53+P         160000         0         N         200         0,20         0,8         50         20 L         2 L         0           4         K3EG4AP         200000         0         N         150         0,20         1,2         70         20         0 </td <td>35.F3A</td> <td>200</td> <td></td> <td>C</td> <td>٦.</td> <td>-</td> <td>15</td> <td>0</td> <td></td> <td>O</td>	35.F3A	200		C	٦.	-	15	0		O
4 K3FE4AP 200000 0 N 150 0,20 1,2 70 20 2 0 3 3 3 5 6 4 K3FE4AP 180000 0 N 150 0,20 1,2 70 30 3 3 0 0 2 1 2 1 2 0 0 8 1 2 1 2 1 0 0 8 1 2 1 2 1 0 0 8 1 2 1 2 1 0 0 8 1 2 1 2 1 0 0 8 1 2 1 2 1 1 0 0 8 1 2 1 1 0 0 1 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 2 1 1 0 0 8 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	36834	6009		0	2	•	20	ာ		
3 K3FE4APX 180000 0N 150 0,20 1,2 70 30 3 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	35E4A	0000		A)		•	70		~	
2 K3FE46P 120000 0 N 300 0,15 0,8 30 20 L 2 L 0 X3FE3AP 100000 0 N 500 0,16 50 20 L 2 L 0 0 X SE6AP 50 0,8 15 20 L 2 L 0 X3FE5AP 5000 0 N 700 6,07 0,8 15 20 L 0 N 0 K3FE68PX 5000 0 N 1000 0,10 2,4 30 20 L 2 L 0 0 X 3 C C C C C C C C C C C C C C C C C C	35.E4A	8000		ŝ	~	•	70	0	~	
3 K3FESAP 100000 0 N 500 0,10 0,4L 50 20 L 2 L 0 0 K3FESAP 5400 0 N 500 0,03 0,8 15 20 L 0 N 0 K3FEAPX 54000 0 N 1000 0,10 2,4 30 20 L 2 L 0 0 K3FEAPX 54000 0 N 1000 0,10 2,4 30 20 L 2 L 0	3FE46	2000		0	٦.	•	30	0		
8 K3FEFAP 64000 ON 500 0,03 O,8 15 20 L ON O F3EEFAPX 55000 ON 700 G,07 O,8 15 20 L 2 L O K3čEóbPX 54000 ON 1000 O,10 2,4 30 20 L 2 L O	35E5A	0000		0	=	•	50	0		
6 K36E6APX 55000 0 N 700 G,07 O,8 15 20 L 2 L O S K3cE6BPX 54000 O N 1000 O,10 2,4 30 20 L 2 L O	35852	400		C	॰	•	1.5	0		
9 K3cEcbPx 94000 ON 1000 O,10 2,4 30 20 L 2 L O	<b>3</b> 5E6A	900		0	0	-	1.5	٥		
	30208	400		0	7		30			
		THE CONTRACT OF THE CONTRACT O	######################################	30.00000000000000000000000000000000000	SAMPLE   SIGN   SIGN	SAME   STATE   STATE	SAVIE   SIGN   Sign	10	\$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	SALES   SALE

APPENJIX V. (continued)

コンコンコンコスコン THE CECTOL Add χB Crscrcrcr 008808080000000 > (continued) 700 **5** Table 3. -- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Wyoming OF JIM BRIDGER # I.I JIM BRIDGER ğ SAGEBRUSH SOUTH SP. PPM WEST 172000 00000 00000 0000 0000 0000 SACEBRUSH \*\*\*\*\*\*\*\*\* 2. 0. 0. 00000000000 000000000000 SI/A PPM 120000 120000 120000 1100000 1100000 100000 72000 190000 16 1000 92 000 62 000 54 000 54 000 92 000 12 000 22 000 92 000 92 000 70 000 SAPPLE LAS. NO. 

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SACERRUSH NORTH OF JIM BRIDGER

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APPEM IX V. (continued)

Table 1 .-- Surface and subsurface soil, and sagebrush at Jim Bridger Powerplant, Myoming (continued)

	Table 1.	Table 1 Surface and	subsurface soil,	and sagebrush at Jim Bridger Powerplant, Wyoming	(cont fr
	.0% .8AJ	SLYPLE	ZN/A PPS	2R PPH	
				SAGEBRUSH EAST OF JIM BRIDGER	
	622	3561	σ	30	
	625	35.5	₹*	50	
	622	3 4 6. 1	~	0	
	625	39.9	7	350	
	ò 25	325	0	20	
	021	35.22	0	30	
	416222	ABPEZEPX	575	30	
	420	E 110	-	7.0	
	£ 23	3863	-	100	
	22,	35E4	9	0	
	621	31:14	~	S	
	621	3024	2	~	
	623	37.55	9	70	
	525	368.5	-	30	
	62.5	35.26	œ	50	
	625	3FE5	N	100	
				SAGEBRUSH SOUTH OF JIM BRIDGER	
3					
o	1624	3-51 A	m	70	
	1625	35516	4	50	
	1022	3652AP	C	70	
	1 £ 2 3	37.524	m	70	
	1522	37524	-	30	
	1623	34534	ď	10	
	1624	38335	÷	70	
	1620	3754A	^	30	
	1625	35347	m	94	
	416240	* 3PS54P	255	. 05	
	1622	3+558	~	150	
				SAGEBRUSH WEST OF JIM BRIDGER	
	1621		C		
	400	37.13	• >	-	
	1623	38 4 2 A	LO		
	1524	38 428	m		
	1623	38 1.3 A	~		
	1:23	37.4 33.	•		
	1521	38 44 A	Œ		
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	416243	£31.45AP	140	150	
	1521	33×56	4	S	
	1622	35 · 6 A	<b>~</b> 1		
	1625	38.68	^		
	1520	33768	-		

APPROTX V. CHEMICAL ELEMENTS IN VEGETATION AND SOIL NEAR COAL-FIRED POWERPLANTS, WESTERN ENERGY REGIONS (continued)

Mexico
Nev
Powerplant,
Corners
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southeast
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and
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	TOTAL CA		0.59	0,61	~	0.46	95.0	0,53	0.41	0,33	0.30	0,36	0.56	0.57	?	0.25	~	60.0	0,13	0.21	0.22	0,25	0.17	80.0	0,22	0.25		9	'n	9
	BE PPM=S			-				2					-														Z 0		-	Z
	BA PPM.S		700	700	100	700	700	700	700	700	1000	700	700	1000	700	200	700	1000	1000	1000	1000	100	700	700	1000	700	700	700	700	1000
	B PPM=S		5	<b>5</b>	z 0	15	5	15	1.5	15	1.5		2	15	15	50	2		1.5					2		5.	Z 0		5.5	15
	AL203 &	CORNERS	0.6	r.	9,1	8,5	œ.	5 6	7,5	7.7	9,4	10.1	10,9	10.9	7,8	7.2	9,9	6,7	O. 8	7,5	7.9	7,5	8,4	6.4	10,4	10.5	7.7	6.9	4.8	9.6
	<b>5 • 5</b>	FOUR	~	~	<b>e</b> n	۰۵	m	m	m	m	ĸ	m	ss	١S	١ſ	m	~	m	ហ	¥۵	N)	ហ	•	~	١C	ъņ	~	m	ĸ	<b>s</b> 0
Powerplant, New Mexico	KM AL	SOIL SOUTHEAST OF	1,50	1,50	1.50	1.50	4.00	4.00	00.4	00	7,50	7.50	7,50	7.50	15,50	15,50	15,50	S	26.00	26,00	6.0	•	•	50,75	ċ	•	0.9	96.00	0	00.96
Four Corners Powe	LONGITUD	SURFACE 8	8	8	~	88	56	108 26 45#	56	~	24	24	24	74	21	7	7	21	7	4	7	7	0	0	0	0	33	~	33	107 33 50M
southeast of	LATITUDE		41	41	4 1	41	40	36 40 42N	40	<b>4</b>	99	6	39	39	37	37	37	37	33	33	33	33 1	24 0	24 0	24 0	24 0	14	14 1	14 2	
Table 4 Soil and grass	SAMPLE		FC1S1A	FCISIAX	FC152A	FC1S2AX	FC251A	FC2S1AX	FC252A	F22S2AX	FC381A	FC3S1AX	FC352A	FC3S2AX	FC4S12	FC4S1AX	FC4S2A	FC452AX	FC551A	FC551AX	FC552A	FC5S2AX	FC6S1A	FC651AX	FC652A	FC6S2AX	FC751A	FC7S1AX	FC7S2A	FC7S2AX
Table 4.	LAB. NO.		169954	169973	165943	169955	169932	169934	169939	169942	169930	169977	169935	169972	169974	169952	169945	169965	169976	169971	169968	169970	168937	169956	169929	169938	169940	169951	169959	186691

APPENDIX V. (continued)

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Corners Powerplant, New Mexico (continued)	FOUR	対し こうじょう こここう うこここう うここここ こうこう こうこう こうこう こ	
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it of		00000000044000000000000000000000000000	
Southeas			
Teble 4Soil and grass southeast of Four B. ND. SAMPLE CA 8-5 C)		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
Table 4		312 313 314 315 316 317 317 317 317 317 317 317 317	

APPENDIX V. (continued)

Table 4.	Table 4 Soil and grass southeast of	southe		OUT C	orners Pot	verplant	New M	Four Corners Powerplant, New Mexico (continued)	(panu								
LAB, NO.	SAMPLE	H	9 9 3:	×	8.4	K20	•	LA PPM-S	ij	W dd	ŭ	S	O U		Z. C.	PPM.S	0 2 8
					SURFACE	SOIL S	SOUTHEAST OF	AST OF FOUR	CORNERS	wa							
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16991	XVISIO				۰ ۳							•	• •	,		0 0	•
159943	FC1S2A		0.0		۰,		2.5	; <b>z</b>		9		0.30	• 0			000	
169955	FC 152AX		0.0		. ~					4		-				0 16	
169932	FC251A		0.02		0		2.2	2		9		0.20	0	35		000	0.02
169934	FC251AX		0.02		7		2,2			11		0.30	0	7		150	0
169939	FC232A		0.01		. 74		2.2	2		13		0.20	0	~		100	0
169942	FC252AX		0.01		~		2.3			<u></u>		0,20	0	~		100	•
169930	FC351A		0,01		~		2.4			*		0,30	0	4		150	0
169977	FC351AX		0,01	•	2		2,5			4		-	0			150	0
169935	FC352A		0.011		8		2,3			16		w	0	9		200	٥
159572	F.352AX		0.01		<b>~</b>		2.4			15		in	0	9		200	0
169974	FC451A		0.01		7		2.4			=		0,30	0	~		200	0
169952	FC4S1AX		0.01		~		2,4	<b>X</b>				2	0	25		150	0
169945	FC452A		0.01		~		2,3					~	0	~		150	0
169965	FC452AX		0.01		7		2,3	<b>z</b>		12		~	0			150	0
169976	F2551A		0.015		~		2,4	30		10		10	0	~		200	•
169971	FC581AX		0,011		<b>~</b>		2.4	<b>Z</b>		01		-	0			150	0
169968	FC552A		0.01L		•		2,5			01		$\sim$	0	7		150	0
169970	FC5S2AX		0,01		~		2,4			10		N	0	. 12		150	0
169937	FC651A		0.01		~		2,3			12		-	0	7		150	0
169956	FC6S1AX		0,011		7		2.4	2		=		0,10	0	7		150	0
169928	FC682A		0.02		<b>~</b>		3.2			13		~	0	20		200	0
163938	FC6S2AX		0.01		т		7.00	2		13		-	0	61.		200	0.0
169940	FC751A		0.01		~		2.8	30		17		-	•	-		200	0
169951	FC7S1AX		0.01		~		2,9	<b>z</b>		11		-	0	13		150	0
169959	FC752A		0.03		~		2,9	0		14		0.30	0	,32		200	0.021
6	FC752AX		0.01		m		2.9	90		14		~	•	181		300	0.02

APPENDIX V. (continued)

Table 4. -- Soil and grass southeast of Four Corners Powerplant, New Mexico (continued)

<i>S</i> 2			٥			• •		•	<b>.</b>	<b>,</b>		<b>,</b>	<b>,</b>	<b>,</b>	<b>.</b>	<b>.</b>		<b>)</b> c	, c				. ~						,	<b>.</b> ~
S-HOPH-S			1.5	-	-			•	1 -	•	• 6	) ¥	י ה	2 6	) v	1 -	•	•	000	· ·	200	200	301	25.			•		3	900
**			78	08	74	78	76	00		76	9	0 00	. ~		) <u>-</u>			2				08		00			, r		• 0	. O
SIDS																						_			•		•			- (-
X dd			70	20	08	75	<b>2</b> 0	70		76		90		70	9	7.1	79	69	70	89	89	69	0 8	79	100	104	98	9.		9 9
8																														
SC PPM-S			2	2	~	~	0	~	0	-	~	× 0	~	~	64	20	Z.		<b>~</b>	<b>64</b>		×	Z 0	-	~	~	~	~	-	
PB PPM=S	CORNERS		0	0	<u>-</u>	0	9	0	0.	10	<u>.</u>	0	0.	15	0.7	<u>.</u>	01	10	2	0	<b>9</b>	0	0	0.	15	0,7	<b>S</b>	<b>9</b>	15	15
NI PPR-S	OF FOUR	•	7	7	- P	~	7	~	~	7	~	<b>~</b>	m	w	~	~	~	~ ∶	in .	~	~	~ (	<b>N</b> 1	7	7	<b>~</b> •	<b>2</b>	<b>z</b>	~	ın
NB PPM S	SOIL SOUTHEAST	6	<b>2</b> 2	<b>2</b> 3	z :	z :	<b>Z</b> :		<b>z</b> :						2			<b>z</b> :	2 2		z		<b>z</b> :					2		<b>Z</b>
*	SURFACE	9	. 4	? <	•		2 0	2 (	3.6	2	2 (	7.	~ 6	2 6	67.	9 0	9 0	<b>N</b> C	2 0		2 0	9 6	2 6	2 4	9 4	10 to	n (	× ×	5	0 <b>m</b>
NA20	SU	-	• -	• •	• •	. ·		٠,	<b>-</b> ∙	Ĭ.	٠.		-₹.	- <b>.</b> .	<b>-</b>	₹.	<b>-</b> -	-	: -	-	<b>:</b> -	: -	-	•	:.	÷.	•	:	~	-
<b>S</b> • • S		1.0			2		•	) r	•	•	-	•	2 u	0.0	) r		•		2 0									•	o •	0
K K																														
SAMPLE		FC1S1A	FCISIAX	FC152A	FC152AX	FC2S1A	FOSTAX	F - 7 G 2 A	F.252AY	FC3S1A	FORSTAX	FC352A	F C 3 S 2 A X	A + 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2 - 2	F) 45.4 AX	FC452A	FC432AX	FC551A	FCSSIAX	F2552A	FC552AX	FC6S1A	FC651AX	F2652A	FC6S2AX	FC781A	FC7S1AX	Fr742A	> c c u c u c u c u c u c u c u c u c u	V 7 5 / 7 .
cas, No.		169954																												

APPENDIX V. (continued)

	S = X d d		•	2 6		9 1	0 0	200	2 6	2 1	) C		000		200	000		0 0	9 6		0 0		0 0		) (		) (	200		200	200
	<b>7</b>																														
	£dd		2	9 6	N (	2 6	2 6	4 C	3 6	<b>7</b> (	7 0		, ,	7 4	0 0	<b>?</b> (		, ,	9 6	2 0	• •	2 0	, ,	• •			3 4		0 :	-	
	N Z																						•								
	PPH=S		0		-	<u> </u>				•	20	•	-			•		•	•	•							•	•	-		· •
	YB P																														
	S-Mdd		0	9	· -	2 5	2 -	2 5	: =	2 -	2 0				2 0	•	2 =	2 -		2 0	: <del>-</del>	· -	-	· •			: =	• •	) <u>.</u>		c.
	<u>~</u>																														
	PPM-S.	Š	20	, <del></del>	2 5	0 6		2 6	. v.	. v	202	R		) C	000	4 <del>-</del>	202	15	0	0	000	<u>د</u>	9 40	5	· •		<u>.</u>		3 0	) (	2
(pen	>	CORNERS																													
(continued)	¥	FOUR	2.1	2.1				2.4	8		2.2	2.0	2		œ		1.7			4	5.5	4		00	0		0				0 8 7
fex 1co	Þ	AST OF																													
New 1	*	SOUTHEAST	N	. 26	~	, ,-	3	0.27	20	2	0.30	-		~		7	•	7	-	-	. 21	11	53	~	m	ñ	28	200	64	•	
Corners Powerplant, New Mexico	TIOS	SOIL S	0				• •		0			C	0				•			•	C	0	0	0	C		C	·c	•		
ners Pov	5) *	SURFACE	0.15		0.15	-		-	٦,	-	, <del>_</del>				-		:	-	7	-	7	7	7		٦.	7		-	20	٠-	•
	H	Ñ				_			_	_	_	_	_	_		_	_	_	_	J	_	_	Ŭ			_	_			, .	
ist of F	g X		8.9	7.1	8.	. 9	5.2	5.4	0.0	5.3	7.3	6,5	7.6	7.7	5.5	9.	9,9	6.1	6.9	5,7	5,4	5.1		7.4		8.7	8,8	6.2	9		•
souther	<b>1</b> H																														
Table 4 Soil and grass southeast of Four	SAMPLE		FC1S1A	FC1S1AX	FC152A	FC1S2AX	FC251A	FC2S1AX	FC252A	F2252AX	FC351A	FC3S1AX	FC352A	FC352AX	FC451A	FC451AX	FC452A	FC4S2AX	FC551A	FC551AX	FC552A	FC552AX	FC651A	FE6S1AX	FC6S2A	FC6S2AX	FC7S1A	FC7S1AX	FC752A	FC7324X	
Table 4	LAB, NO,		169954	169973	169943	169955	169932	169934	169939	169942	169930	169977	169935	169972	169974	169952	169945	169965	169976	169971	169968	169970	_	169956	169928	169938	169540	169951	169959	149981	•

APPLINGIX V. (continued)

(continued)

Mexico

Nev

Powerplant,

southeast of Four Corners

and grass

Table 4. -- Soil

TOTAL Z ZZZZZZZZZZZZZZZZZZZZZZZZ PPK .0000000000000000000000000000000000000 BE SEXAG ă z ZZ ZZZZZ Z ZZ S-Edd **6**0 \$\\ \partial \text{app} \text{app CORNERS AL203 CF FOUR S-SOUTHEAST AL X SOIL SUBSURFACE LONGITUD LATITUDE SAMPLE LAB. NO. 36

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APP NDIX V. (continued)

	×dd		0,01	0.0	10.0	0,02	0,02	0.01	0.011	0.01L	0.02	0.011	0.011	0.01	0.011	0.02	0.01	0.02	0.02	0.01	0.02	0.01	710.0	10.0	0.02	0.01	0.0	0.01	0,01
	×																												
	GA PPM-S		~;	- 1-		1	^	4	7	_	7	9	7	IIO	7	7	7	^	7	_	1	7	-	_	10	1	w	10	,
	S • 4		0.		0	0.7	6.7	0.7	٥,	. 0	0.7	0	0.0	0.7	0.7	0.7	0.1	0	0.7	0.0			7.0	0	0.1	0	0,7	•	6.0
	3																												
	•		0.04	0.0	0.041	0,04L	0.04L	0.04L	0.04L	0.045	0.05	0.045	0.041	0.04L	0,05	0,05	0.041	0.041	0.041	0.041	0.041	0.041	0.0	0.041	0.041	0.041	0.04	0.0	90.0
	ia.																												
ed)	CU PPM-S	CORNERS	IO E	- un	ı vo	ĸ	<b>S</b> O	•	un	so.	ĸ	^	S.	~	7	ĸ	<b>5</b> 0	m	m	m	~	~	m	m	m	_	~	10	un
lexico (continu	CR PPRES	BSURFACE SOIL SOUTHEAST OF FOUR CORNERS	01	- 1	10	1	_	7	7	_	ъņ	10	ĸ	<b>a</b> n	un	~	7	ъn	un	<b>₽</b> O	w	un	w	7	7	7	7	1.5	w
werplant, New M	CO PPM-S	E SOIL SOUTH	20	N (*	· ~	2	m	~	~	~	~	S.O.	7	7	8	~	~	~	۲۹	~	~	~	~	•	~	~	7	ທ	8
ers Po		SURFA	80	10.0	1.66	114	1,16	0,84	986	. 15	.77	73	7.1	58	57	61	. 61	63	56	09.	.57	41	. 47	71	.71	35	, 32	98.	06
Pour Corr	CAO	SUB		-1	•	_	-	0	0	0	0	0	0	0	0	0	0	0	•	0	0	0	0	0	0	0	0	•	0
east of	S		L.	0.00	٠,	۲.	۲.	ĸ.	2	~	3.	ď	ď	٣.	~	~	~	٣.	٣.	~	٣.	٣.	~	'n	S	۲.	٦.	~	<u>.                                    </u>
south	ฮ																												
Table 4, Soil and grass southeast of Four Corners Powerplant, New Mexico (continued)	SAMPLE		F (C)	FC1528	FCISZRX	FC2513	FC2518X	FC2528	F22528X	FC351B	FC3518X	FC3528	FC3528X	FC451B	FC4S1BX	FC4528	FC452BX	FCSS18	FC551BX	FC5528	FC5528X	FC6518	FC6818X	FC6528	FC652BX	FC7518	FC7515X	FC7528	FC7528X
Table 4.	CAB, NO.		169950	0.0000	169947	169926	166591	169946	169964	56651	169958	169967	169962	169927	169953	189951	169949	169960	169933	169969		£96691 37	169948	169936	196691.	7	2	169966	ec ec

APPENDIX V. (continued)

**S=** 

	4												•																	
			.02L	1020	,020	026	,021	0,024	.02L	021	.02L	021	,02L	020	1001	021	.02L	, 02L	.02L	*02F	,02L	024	,02L	.02L	50.	<b>0.</b>	,02L	.02L	027	.02L
	ONK		ō	0	0	0	0	0	0	0	0	0	0	0	0	٥	0	ō	o	o	ō	0	0	0	0	0	0	0	0	0
	REMUTE NA		150	200	051	150	150	150	001	150	200	150	200	150	150	150	150	150	150	100	150	150	150	150	00E	00 <b>E</b>	200	150	300	150
	•		0.47	0.45	0.43	0.42	0,37	0,36	0,27	0,28	0,26	0.26	0.27	72.0	0,25	0,25	0,27	0.28	0,19	0,18	0.18	0.17	0,15	0.14	0,21	0,22	0,14	0,15	0,34	0,033
	MGO				`																									
	S	CORNERS	0.30		0.30	ຸ ຕ	0.30	0.20	0,20	0,20	7		٣.	0,20	~		~	~	0,15	7	٦.	0,15	٦.	0,10	~	~	0,30	಼	0,30	~
(penu	Ĕ																													
(continued)	g. M	OF FOUR	7 9	** **	· ~	-1	1.6	9:	11	13	12	~	11	13	=	=	12	=	23	12	=	12	10	11	13	1.	0.	11	14	14
Mexico	13	THEAST																												
Four Corners Powerplant, New Mexico	LA PPM-S	E SOIL SOUTHEAST	0	2	2	2	2	2	2	0	2	2	30	2	2		30	20	2	-	-			-				20		<b>Z</b>
ers Pow	*	SUBSURFACE	2,3	2,3	2,3	2.3	2.3	2,3		2,3		2.4	2,5		2,3	2,3	2,3	2,3	2.4	2,3	2,4	2,3	2.3	2,3	3,0	9.0	2,8	2,6	8.8	2.9
Four Corn	K20	808																												
딍	5=2		~	•	150	7	~	~	~	~	~	~	~	~	~	~	~	~	~	~	~	~	~	~	~	m	~	~	m	m
southe	×																													,
Table 4 Soil and grass southeast	SAMPLE		FC151B	FCISIBX	FC1528	FC152BX	FC2518	FC251BX	FC252B	FC2S2BX	FC351B	F_3518X	FC3528	FC3S2BX	FC4518	FC4518X	FC4528	FC4528X	FCSS1B	FCSSIBX	F2552B	FC5S2BX	FC6518	FC6518X	FC6528	FC6528X	FC7518	FC781BX	FC752B	FC7S2BX
Table 4	LAB. NO.		169950	169975	169944	169947	169926	169931	169946	169964	159979	169958	169967	169962	169927	169953	169957	169949	169960	169933	169969	_	169963	169948	169936	169961	169978	169929	169966	169980

APPENDIX V. (continued)

Table 4 .- - Soil and grass southeast of Four Corners Powerplant, New Mexico (continued)

A d d		7.9	6.3	•	5.2													5.7			5.5		7.6					<b>4</b>	
¥																													
SP PPH S		150	150	100	150	100	100	001	100	001	200	150	150	100	001	001	100	150	150	150	150	150	100	200	150	200	10	150	150
*		78			75		77	78	693	90	82	83	08	7.8	08	18	78		76	 	78	18	9.6	70	77	82	18	78	7.8
\$102				٠																									
Æ		79			79				69			70	70	16	7.1	7.3	16	71	19	70	81	63	79	6	46	08	i~1 00	 60	90
S X																													
SC PPR	CORNERS	•	7	m	m	0	m	0	~	~	2	m			0			~		20		~	2	6	m	~	2		0
PR PPM.S	EAST OF FOUR	10	15	01	01	10	10	0.7	10	15	10	15	0.1	10	0.7	0.7	10	01	01	10	9	10	10	15	15	1.5		50	
S-Wdd IN	E SOIL SOUTHEAST	•	~		~	~	~		<b>Z</b> .	~	~	ı,	~	۲۰	~	~	~	7	~	~	~	~	~	~	~	~	~	**	ın
NB PPM-S	SUBSURFACE	0		_	2																			-				z 0	
NA20 &		1.55	1,53	1,36	1,31	1.20	1,20	1,25	1,25	1,51	1,55	1,44	1.46	1.20	1,26	1,25	1,25	1,35	1,30	1,40	1,41	1,09	1,28	1,61	1,68	1,08	0,93	1,33	1,31
SAMPLE		FC1519	FCISIBX	FC1525	FC1S2BX	FC2SIR	FC251BX	FC2525	FC2S2BX	FC3S1B	FC3518X	FC3528	FC352BX	FC4518	FC4518X	FC4528	FC432BX	FC5518	F25S1BX	FC5528	FCSS2BX	F26518	FC651BX	FC6528	FC6526X	FC7518	FC751BX	FC7528	FC7528X
LAB. NO.		169950	169975	169944	169947	169926	169931	169946	169964	169579	165.58 1	169967	169962	169927	169953	169957	169949	169960	169933	169969	186691	169963	169948	169936	19661	169978	169929	169966	169980

APPENDIX V. (continued)

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88 \$\$ TOTAL E O ñ FOUR CORNERS (continued) ١. PPM Table 4 .- - Soil and grass southeast of Four Corners Powerplant, New Mexico AS 9 SOUTHEAST ¥ GRASS LONGITUD ちろころころころころころこと ちょしゅうしゅう ちろろろろろころころころころこと ちょうしゅん ちゅうしょ カルト・しょ カルト・ション ジャン・ファイト しょう カルル・ウェン こうしょう しゅうしょう しゅうしゅう しゅうしょう しゅうしょう しゅうしょう しゅうしょう しゅうしょう しょうしょう しょうしゅう LATITUDE SAMPLE LAB. NO. 

APPENDIX V. (continued)

Table 4. -- Soil and grass southeast of Four Corners Powerplant, New Mexico (continued)

CO/A PPH			4,2	0.7	3,2	, co	2.4	-	7.	7 6	2,0	3.2	, m		•	-	3,2	9,6	3,2		9		7	*	3,2	1.4	2,8			9	2,8	*•	**	2.4
CD/A PPH		•	•	7,4,0	1,6	0.1	0.41		-	•	70.1	0.45	4.0	0.1	•	<b>0</b>	*.0	0,40	0.1	1.0	4			20.	D	œ د	**	0.41		•	•	1.2	1.2	0.1
*		,	0	2.	8.9	9,9	5.2			•	2	7.2	9.9	5.6			2	9 .	7,6	7.4	9.9	,,		•	•	<b>6.</b>	9,5	9.9	9.9		•	2,5	4.4	7,
CA/A																																	•	-
8-8		5		<b>)</b>	201	07	ເດ	,	• •		9 (		10	10	-	•	<b>&gt;</b> •	01		0	10	10	, •	۰,	٠:	D 1	_	9	20	, -	- 1	_	7	~
ర																																		
BA PPM-S	ERS	4		0061	0001	1500	200	1000	1500	004	9 6	0001	1200	1000	1000	9 6		000	002	100	1500	1500	1000			0061	0061	1500	1500	1000		000	1000	700
PPM-S	FOUR CORNERS	006			9 6	007	200	300	200	300			007	200	200	200		2 4	0 1	150	150	150	200	000	0 0	9 6	9 1	200	150	100		) (	0 1	150
α,	T 0F																																	
\$ • S	SOUTHEAST	9			•	2	7	0	5,0	S	~		2 1	20	5,0	3.0	· ·				0	0	2.0	2.0				ָ ה ה	0	5.0			2	o •
A L	SS SOL																																	
AG PPM=S	GRASS	NO.0	20	200			50	Z 0 0	K0 0	NO.0	NO.0			20 0	NO.0	. O.	20	200		2000	NO 0	20.0	×0.0	NO.0	20.0	200		- i	NO 0	20.0	NO.O			ž 0
		7.7	6.5					0	9 6	0.8	0,0		2 (	) ·	2.0	7,1	. 9		· ·	2	- '	<b>10</b>		5,1	7.3		· a		7.		5.4			0
ASH							•	~					•	• •	-														.,	•	_	•		-
SAMPLE		FC1GA	FCIGAX	F.2169	FAIGHX	F. 7.7.8	> < t < t < t < t < t < t < t < t < t <	\$ 10 0 0 1 L	10208	FCZGBX	FC3GA	× 60 m 0 5.	100	> 0 C C C C C C C C C C C C C C C C C C	4055 Jul	FC40A	FC4GAX	FC4GB	FC4GBX		> C C C C C C C C C C C C C C C C C C C	< :	S	FESCBX	7.56A	FC6GAX	F1668	X 0 0 0 1	6 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	4 5 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	FC7GAX	F: 7GB	Ye 7 Ca X	
LAB, NO.		416644	416660	416657	416656	416653	4.468.	7777	7007	#1001 <b>+</b>	416663	115661	416652	4.46.5		415662	4165.3	416615	416653	41464.	416647		0/00/1	41.6649	410563	415664	416654	416646	2007	0001	4:6666	416667	416548	•

APPENDIX V. (continued)

PPM.S

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\$ .. S

Ä E O LI/A . K/X 00000000000000000 \*\* G 0 0000 OF FOUR CURNERS Table 4.--Soil and grass southeast of Four Corners Powerplant, New Mexico (continued) × GA PPM=S GRASS SOUTHEAST S (d) (d. PPMeS Ö CR PPM-S SAMPLE LAB, NO. 416664 416664 4166653 4166653 4166653 4166653 4166653 416666 416666 416666 416666 416666 416666

APPENDIX V. (continued)

Table 4 . - Soil and grass southeast of Four Corners Powerplant, New Mexico (continued)

9-4		0.10	0.15	0.10	0.15	0.0	0.07	010	0.10	0,10	0.10	0.07	0.10	0.10	0,10	0.03	0.05	0.07	0.07	0.07	0.07	0.10	0.10	0.10	0.07	0,15	0.15	0.15	0.07
H																													
SR PPMes		700	700	100	100	100	1000	100	700	1000	1000	700	200	200	200	100	700	200	300	300	300	200	200	700	700	300	300	300	200
SI/A PPM		190000	210000	210000	210000	200000	210000	210000	<b>6</b> 0	220000	220000	220000	250000	210000	190000	160000	170000	250000	260000	240000	250000	270000	260000	250000	250000	280000	230000	260000	300000
PB PPM-S		9	0	30	80	20	20	30	30	30	50	20	30	30	30	<b>Z</b>	<b>5</b> 0	980	50	30	50	30	50	30	30	50	30	50	0 10
P/A PPM	- SERS	0009	9009	9000	0009	0006	12000	0006	0006	9009	0006	0006	0006	0006	0006	12000	12000	0009	0006	0006	12000	0009	6000	0006	6000	0006	12000	0009	0009
S.	FOUR CORNERS	1,5	1,5	1,5	0.1	1,5	2,0	1,5	2.0	1,5	1,5	1.5	20.00		2.0	0	2.0	1,5	1.5	1,5	2,0	1,5	1,5	1,5	1.5	2,0	2,0	 	1,5
۵.	6																												
NI PPR-S	GRASS SOUTHEAST	30	°.	50	15	_	10	15	-	01	01	10	~	7	0.7	07	15	7	21	_	2	7	7	7	7	0,	0.7	w.	ın
NA/A *	GRAS	. 0,24	0,22	0,15	0,19	0.24	0.17	0, 1R	0,15	0.14	0,11	0,12	0,11	60.0	0,11	90.0	90.0	90.0	80.0	0.07	0.07	0,15	0,10	0,15	0,15	80.0	80.0	80.0	0.07
MO PPM.S		30	30	1.5	20	20	30	30	20	30	30	20	20	50	1.5	30	20	1.5	~	10	1.5	5	2.5	1.5	۲	10	25	2	<b>r</b>
SAMPLE			E3	EJ	63	E)	w	E)	E)	Ł	()	w	u	3	3	€.			€,	1,	u	L)	u	t)	E.			FC768	.,
LAB. NO.		416644	416660	4:6657	4;5656	416653	416651	416643	416658	416663	416461	4:6652	416669	416662	416659	416655	416650	416645	416647	416670	416649	416668	416564	416654	416646	416665	416666	416667	416648

APPENDIX V. (continued)

APPENDIX V.	V. (continued)								19		
- 4 444	Table 4 Soil and grass southeast of Four Corners Powerplant, New Mexico (continued)	southeast of	Our C	orners Por	verp1	ant, New h	ex 1co	(continu	ed)		
CN di	SAMPLE	MAG. Y/n	>	S-Wdd	>	PPH-S	ΥB	PPH=S	ZN/A PPM	Z Z	NG G
_				GRA	SGS	GRASS SOUTHEAST	0.F	FOUR CORNERS	ERS		
								•	•		6
	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	c		90		<b>z</b>		20.0	0 7 7		) (
416644	FC164	•				<b>S</b>		'n	120		- 1
415560	FCIGAX			2 6		. <u>.</u>		ic.	110		70
4.6657	F 1 68	8.0		0		) W		0.0	110		100
4 6 6 5 6	FCIGBX	0.4		7.0				2	170		<b></b>
	4000	<b>7.</b> 0		50				200	180		200
	March College	4.0		30							100
	1 C C C C C C C C C C C C C C C C C C C	8.0		20		z :					70
9 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	> d	0.08		<b>3</b> 0							7.0
8 C Q Q T *	<	, c		50				0	n		
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416661	F 3 3 5 4 X							NO.	110		- 1
416652	FC368	e (		) (		z.		NO.C	001		2 1
416669	FC3GBX	в (		) C		100		1.5	08		0.1
416662	FCAGA	œ (		) (		. <del>.</del>		35	06		2
416659	FC4GAX	7		0 0				NO.O	120		
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416650	FC4GBX	3 ° °						NO	75		2
416645	FC5GA	8 0		2 0				NO.0	80		-
416647	FCSGAX	1.2		) (				20	110		2
4:6670	FC5G9	1,2		2 6				20.0	06		200
416649	FCSGBX	a .		7 1		F		1.5	700		-
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